

Environmentally Assisted Cracking: Science and Engineering

Lisagor/Crooker/ Leis, editors



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W. Barry Lisagor, Thomas W. Crooker, and Brian N. Leis, editors



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The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of these peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and contribution of time and effort on behalf of ASTM.

Foreword

The ASTM Symposium on Environmentally Assisted Cracking: Science and Engineering was held in Bal Harbour, Florida, on 9–11 Nov. 1987. The event was sponsored by ASTM Committees G-1 on Corrosion of Metals, E-24 on Fracture Testing, and E-9 on Fatigue. The symposium chairmen were W. B. Lisagor and T. W. Crooker of the National Aeronautics and Space Administration, and B. N. Leis of Battelle Columbus Laboratories. This publication was edited by Mr. Lisagor, together with Messrs. Crooker and Leis.

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Overview

The Symposium on Environmentally Assisted Cracking: Science and Engineering was organized to assess progress in the understanding and control of this phenomenon, recognized as one of the most serious causes of structural failure over a broad range of industrial application. This mode of failure continues to pose a long-term concern for the use of metallic materials in applications involving aggressive liquid and gaseous environments throughout the range of service temperatures. Research into environmentally assisted cracking has continued to progress in recent years. ASTM has previously held a series of symposia on various aspects of this phenomenon, most recently in April 1982 (see ASTM STP 821). With the continuing research on this important cause of metal failure and new service applications placing increasing demands on metallic structures, the organizers from ASTM Committees G-1, E-24, and E-9 recognized the need for another broad-based symposium addressing both the science and the engineering aspects of the subject. The resulting symposium was held 9–11 November 1987 in Bal Harbour, Florida.

Papers were solicited on a range of topics that included phenomena, basic mechanisms, modeling, test methodologies, materials performance, engineering applications, and service experience and failures. This volume reflects the current emphasis with regard to material/ environment systems, research community addressing the topic, and specific technical interest. The content suggests that the subject continues to cover the broad spectrum of structural alloys and environments as well as numerous test methods and approaches.

As a result of the invited presentations, the symposium was organized into six sessions, including sessions addressing mechanisms, modeling and analysis, and test methods; and three sessions addressing material performance to specific service environments. It is anticipated that a greater appreciation of all aspects of this complex phenomenon, mechanical as well as chemical and electrochemical and their interaction, will be derived from the information presented; and that no single preferred test technique or concept will likely emerge in the future but that all will contribute to a better understanding of materials behavior.

The editors would like to acknowledge other members of the symposium Organizing Committee who contributed to the content of the symposium as well as this publication and who served as chairmen of various symposium sessions. They include: D. O. Sprowls, Committee G-1; R. P. Gangloff, Committee E-24; and C. Q. Bowles, Committee E-9. We would also like to extend sincere appreciation to the ASTM staff, both technical and editorial, for their diligent efforts in the conduct of the symposium and the preparation of this publication.

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Mechanisms

Influence of Strain on Hydrogen Assisted Cracking of Cathodically Polarized High-Strength Steel

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ABSTRACT: Evidence is presented that confirms the role of mechanical strain in promoting surface absorption of hydrogen in two high strength steels under cathodic polarization in alkaline 3.5% sodium chloride solution. Data are reported for a 5Ni-Cr-Mo-V steel {896 MPa (130 ksi) yield strength} and is compared to data previously developed for AISI 4340 steel $\{1207 \text{ MPa } (175 \text{ ksi}) \text{ yield strength}\}$. Strain induced bare surface generation is shown to substantially influence both alloys' hydrogen cracking susceptibility. Strain enhanced absorption is empirically observed for tensile specimens under slowly straining conditions and is also suggested to explain the hydrogen assisted cracking behavior of slowly strained DCB compact and cantilever beam fracture mechanics specimens with pre-existing fatigue cracks. Enhancement of hydrogen absorption per unit area of bare surface, as determined by straining hydrogen permeation measurements, explain the effect. In the presence of a corroded surface, the kinetics of the hydrogen evolution reaction are modified such that a lower cathodic hydrogen overpotential is observed at a given cathodic current density. This lowers hydrogen absorption at a given applied cathodic current density. Hydrogen permeation rates are increased upon straining independent of changes in the apparent bulk diffusion coefficient. These findings indicate that sustained plus cyclic loading and low-cycle fatigue of steels in seawater are more severe environmental cracking conditions than sustained loading typical of laboratory cantilever beam tests.

KEY WORDS: cracking, environmental effects, adsorption, absorption, diffusion, corrosion, cathodic protection, cyclic loading, dislocation transport, fatigue (materials), film rupture, embrittlement, high strength steel, hydrogen, hydrogen embrittlement, hydrogen evolution, hydrogen permeation, seawater, stress corrosion cracking, sustained load, threshold stress intensity, trapping

The hydrogen assisted cracking of high-strength steels in sodium chloride solution has been shown to proceed in four distinct stages [I-4]. These include an incubation stage, cracking initiation, crack propagation, and crack arrest. During incubation, solution transport to the crack tip or pre-existing flaw, electrochemical reaction, hydrogen adsorption, hydrogen absorption, hydrogen diffusion, and hydrogen segregation occur. Cracking initiation in the case of high strength steels occurs in the triaxially stressed region at the position

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of stress concentration where a certain state of stress and segregated hydrogen content simultaneously exist [5]. The threshold stress intensity, $K_{\rm th}$, for hydrogen cracking initiation has been linked directly with the estimated subsurface hydrogen concentration, $C_{\rm o}$ [6–8] through an inverse power law relationship. Under sustained load, dead weight load, or increasing load conditions, hydrogen cracking initiation may temporarily lead to crack arrest or transition to ductile crack propagation as increasing stress intensities promote crack advance into a zone of material initially containing a lower segregated hydrogen content. In the case of a fixed initial crack opening displacement or constant strain, crack advance eventually decreases the operative stress intensity thereby promoting crack arrest. In either case, after crack arrest, additional hydrogen accumulation may satisfy the original criteria for initiation (certain state of stress and certain critical segregated hydrogen content) and the process may repeat. Thus initiation may be considered a key step in the overall hydrogen assisted cracking process for high-strength steels undergoing environmental hydrogen cracking phenomena.

Resistance to the initiation of environmental cracking can be characterized by K_{Isc} , or $K_{\rm th}$, the threshold stress intensity for environmental cracking. At applied stress intensities above this value crack propagation occurs. Empirically K_{th} has been found to vary from 10 to 75% of the inert environment fracture toughness, K_{lc} [7]. In fact, both K_{th} and Region II crack growth rates have been found to be strongly dependent on the following factors for a particular alloy and heat treatment: load rate or strain rate [9-11], prior levels of applied Mode I crack tip stress intensity [12-16], the frequency of the applied delta K, applied delta K magnitude, applied delta K waveform [17-20], the localized environmental composition and impurity level [2,3,21], and the crack tip electrode potential [22-24]. Explanations for such noted variability in $K_{\rm th}$ or Region II crack growth rates have usually relied upon the slow kinetics of one of the discrete sequential steps in the hydrogen accumulation process [25,26]. Many quantitative kinetic models for hydrogen assisted cracking of high-strength steels assume hydrogen diffusion to be the rate limiting process for crack growth [16,27-32]. Dislocation enhanced transport of hydrogen has been postulated [33,34]and investigated as a means of enhancing hydrogen permeation and accumulation [35-46]. The role of surface strain in enhancing hydrogen cracking phenomena through modification of surface absorption has not been thoroughly considered.

Recent work [11] showed a strong influence of the crosshead displacement rate (and crack tip strain rate) on the hydrogen assisted cracking susceptibility of pre-cracked AISI 4340 steel in 3.5% sodium chloride (NaCl) solution. The strain rate (displacement rate) was found to have a strong influence on the threshold stress-intensity value for hydrogen cracking independent of the extent of precharging. Particularly, lower strain rates promoted increased susceptibility and consequently lower-threshold stress-intensity values. Conversely, the extent of precharging under slight load had very little influence on the critical stress intensity value at the higher strain rate. One interpretation of these results is that the increasing stress intensity and crack tip strain ruptures surface films at the crack tip exposing fresh metal surface to the solution which enhances hydrogen absorption. Surface films have been found to alter hydrogen absorption for iron in alkaline chloride solutions [47-50]. The lower strain rate utilized in the study cited previously [11] may have allowed sufficient time after film rupture for hydrogen absorption, transport, and subsequent embrittlement of a zone of material in front of the crack tip. Faster strain rates not only rupture films, but promote rapid increases in the stress intensity, causing ductile crack propagation prior to adequate hydrogen absorption, transport, and segregation. Fractography supported this scenario with the lower strain rate results exhibiting intergranular cracking at prior austenite grain boundaries for a distance that ranged from 400 to 1000 µm ahead of the initial air fatigue crack tip. The fast strain rate tests exhibited only ductile fracture that was also typical for the air tests.

This hypothesis was confirmed by additional studies on AISI 4340 [51,52]. In these tests, straining hydrogen permeation experiments and other slow strain rate studies with and without prior corrosion film formation confirmed that hydrogen absorption rates were enhanced when the corroded surface was either ruptured by straining or avoided in surface preparation. Decreases in ductility were observed when straining and cathodic polarization were applied concurrently.

Strain enhanced absorption may also explain the increased hydrogen embrittlement susceptibility observed in several other studies of steels in seawater under sustained plus cyclic loading or low cycle fatigue [17-20]. All of these studies are linked by the presence of concurrent strain and cathodic polarization in cases where hydrogen damage was maximized. Here, we investigate 5Ni-0.5Cr-0.5Mo-0.05V steel similar in microstructure, composition, and strength to AISI 4340. It has been shown that the hydrogen cracking susceptibility of this steel under cathodic polarization in seawater was markedly increased by high R ratio, low frequency, cyclic loading or low cycle fatigue [18].

Here, we confirm the feasibility of the hydrogen absorption hypothesis developed above for the 5Ni-0.5Cr-0.5Mo alloy. Extensive comparison of experimental results to those obtained for AISI 4340 steel are made.

Experimental Procedures

Materials and Specimen Preparation

Samples were produced from single heats of either 5Ni-0.5Cr-0.5Mo-0.05V steel (Mil-S-24371A), or AISI 4340 steel (UNS No. G43400), both heat treated to form tempered martensite. The AISI 4340 alloy is the identical heat of AISI 4340 utilized in the fracture work described previously [11]. This alloy had a nominal yield strength of 1207 MPa (175 ksi), 10 to 12% elongation, and 40 to 50% reduction in area at failure in air. The 5Ni-0.5Cr-0.5Mo-0.05V steel (Mil-S-24371A) alloy was produced with a 896 MPa (130 ksi) yield strength, 19 to 22% elongation in 5 cm (2 in.) and a 65 to 80% reduction in area at failure in air. Nominal compositions are given in Table 1.

Element	5Ni-Cr-Mo-V ^a	AISI 4340 ^b	
Fe	BAL	BAL	
С	0.13	0.41	
Mn	0.82	0.74	
Р		0.009	
S	0.002	0.016	
Si	0.24	0.21	
Cu	0.05		
Ni	5.20	2.00	
Cr	0.44	0.74	
Мо	0.52	0.26	
v	0.05	0.05	
Ti		••••	
Material code	FYP	FYS	

TABLE 1—Nominal composition (in percent by weight) of AISI 4340 steel and 5Ni-Cr-Mo-V steel.

^a Composition determined by: ladle analysis.

^b Composition determined by commercial laboratory analysis.

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Environments

All electrolytes employed in this study were prepared from reagent grade chemicals and deionized water (5 to 12 μ S/cm conductivity). Electrolytes were 0.6 *M* NaCl adjusted to a specific pH in the range of 8 to 11 with sodium hydroxide (NaOH), or ASTM artificial ocean water at a pH of 8.2 to 8.4 [53]. The alkaline chloride environment was chosen to simulate the conditions created in the occluded crack tip environment of a steel alloy when under the application of external cathodic polarization in a neutral chloride environment. Such conditions have been clearly demonstrated in the literature [22–24,54–57]. All experiments were conducted at a temperature of between 24 and 27°C.

Slow Strain Rate Tests

Three different types of slow strain rate samples were utilized; smooth, tapered hourglass, and notched. Details are illustrasted in Fig. 1. Notched samples were utilized to promote greater strain localization, strain rates, and stress intensification upon loading qualitatively approaching that of the crack tip region of the double cantilever beam specimen of previous studies [11, 18]. All slow strain rate specimens were oriented with the tensile axis perpendicular to the rolling direction of the plate.

Tests were performed at displacement rates ranging from 2.54×10^{-7} to 2.54×10^{-2} cm/s (10^{-7} to 10^{-2} in /s). This produced engineering strain rates of 10^{-7} to 10^{-2} s⁻¹ for the smooth 1 in. gage length samples (prior to necking). The reduction in cross sectional area of the specimen at failure or maximum load or both during test were determined. From the method described by Bueckner [58] the stress-intensity factor at the breaking load was estimated. Given the notch sensitivity of the AISI 4340 alloy, in particular, this stress intensity was considered to be representative of the threshold stress intensity, K_{th} , for cracking initiation at the particular cathodic charging level. During straining, specimens were cathod-



FIG. 1—Slow strain rate test specimen types and dimensions.



FIG. 2—Transient open circuit potential behavior for polished 5Ni-Cr-Mo-V steel in ASTM artificial ocean water.

ically polarized under potentiostatic control. Other details concerning specimen preparation and testing procedures have been previously discussed [51].

All samples were initially exposed at open circuit for a period of less than several minutes. The open circuit potential behavior obtained upon exposure is illustrated in Fig. 2. Using the impedance method, an initial corrosion rate of 40 to $50 \,\mu\text{A/cm}^2$ was estimated. A corrosion film replaced the air formed oxide on all slow strain rate specimens during this period prior to cathodic polarization. This condition was considered to be representative of, for instance, a precracked or notched region of metal under sustained (but not cyclic) load with creep strains only, before cathodic polarization, hydrogen cracking initiation, and exposure to bare metal. Even after cathodic polarization ohmic resistance may limit the initial level of cathodic current at the crack tip under static loading. Subsequent cyclic loading has been shown to produce order of magnitude increases in cathodic currents in addition to increasing crack tip strain [59].

Hydrogen Permeation Studies

The Devanathan-Stachurski technique [60] was utilized to study hydrogen permeation. In all cases the cathodic charging side was controlled at a constant current. These current densities utilized ranged from -30 to $-1200 \,\mu\text{A/cm}^2$ depending upon experiment (in ASTM convention cathodic currents and current densities are considered negative). The cathodic current densities in the low end of this range (near $-30 \,\mu\text{A/cm}^2$) are representative of cathodic protection current densities actually observed per unit area of bare sections of cathodically polarized steel in seawater. As mentioned, transient current increases with strain can far exceed these current densities [59]. Electroless and sputter deposited palladium coated exit surfaces were utilized in all cases. Exit surfaces were potentiostatically controlled in a potential ranging from -550 to -650 mV versus SCE. This potential was sufficiently negative to minimize anodic currents arising from steel dissolution should the palladium be ruptured in the straining experiment. Background current densities of less than -0.1 and $-0.4 \,\mu\text{A/cm}^2$ were obtained in static and straining Devanathan-Stachurski experiments, respectively. In the case of straining experiments, preliminary experiments confirmed that this background current remained cathodic during the period of straining. This background level was subtracted from the exit anodic current density as is the normal procedure. One group of Devanthan-Stachurski experiments was conducted with the specimen instantaneously cathodically polarized while the electrolyte was added. In this manner, oxidation of the surface in the chloride containing electrolyte was avoided (or minimized). This method has been previously discussed [51,52] and is hereafter referred to as instantaneous cathodic polarization, or ICP. Other samples experienced some prior anodic dissolution by corrosion at potentials ranging from -400 to -650 mV versus SCE, consistent with the results shown in Fig. 2 for periods ranging from seconds to hours. Hereafter, this condition will be called slightly corroded.

Specimens were strained at a constant extension rate of 11.43×10^{-7} cm/s (4.5×10^{-7} in./s) (4.5×10^{-7} s⁻¹ nominal engineering strain rate) or 2×10^{-6} s⁻¹ to a total strain not exceeding uniform macroscopic plastic elongation (that is, below the ultimate engineering tensile strength and before the onset of necking). Concerning cyclic straining, the constant extension rate was reversed for time periods of 200 min per cycle. Results are presented for nominally identical test runs conducted in alkaline 0.6 *M* sodium chloride solution at a cathodic galvanostatic charging current density of $-500 \mu A/cm^2$. The transient permeation rise and decay method previously discussed [52,61] provided direct means to verify that the permeation increases reported in Table 2 are not artifacts of background current changes but truly represent increases in the hydrogen permeation rate.

The kinetics of the water reduction reaction were investigated for both steels during the nonstraining permeation experiments under the same conditions described above. Hydrogen overpotentials for the water reduction reaction were determined from measurements of the working to reference electrode potential taking into consideration the measured solution pH.

Results

Slow Strain Rate Tests: Influence of Strain Rate

Figures 3 and 4 illustrate the effects of strain rate at constant cathodic polarization levels for smooth AISI 4340 and 5Ni-Cr-Mo-V steel alloy samples, respectively. The data are presented as percent reduction in area at failure versus strain rate. The reversible potential for the reduction of water in ASTM ocean water is -0.74 V versus SCE. Therefore -0.85V versus SCE (Fig. 3) is a lower overpotential relative to the -1.00 V versus SCE polarization level possible for structures cathodically polarized in seawater with zinc sacrificial anodes [22,51,55,56]. For AISI 4340 steel hydrogen susceptibility is observed at strain rates below approximately 10^{-4} for the -1.00 V level and at lower strain rates for the -0.85 V level. Concerning the AISI 4340 steel alloy at -1.00 V versus SCE, the percent reduction in area decreases from 45% at a strain rate of 10^{-4} or greater to 10% at a strain rate of 10^{-5} or less. Similar behavior is observed at -0.85 V versus SCE except that the percent reduction in area is less substantially reduced at the intermediate and lower strain rates. For the 5Ni-Cr-Mo-V steel alloy, qualitatively similar behavior is observed with the percent reduction in area decreasing from greater than 45% at 10^{-4} s⁻¹ to below 20% at a 3×10^{-7} strain rate at -1.00 V versus SCE.

Figures 5 and 6 illustrate the influence of displacement rate on embrittlement susceptibility



FIG. 3—Relationship between strain rate and ductility for AISI 4340 steel in ASTM artificial ocean water at two cathodic polarization levels.



FIG. 4—Relationship between strain rate and ductility for 5Ni-Cr-Mo-V steel in ASTM artificial ocean water at -1.0 V versus SCE.

for tapered hourglass and notched AISI 4340 specimens. Figures 7 and 8 illustrate the influence of displacement rate on embrittlement susceptibility for the tapered hourglass and notched 5Ni-Cr-Mo-V steel specimens. Qualitatively similar behavior as for the smooth specimens is observed in that less environmental damage is observed at crosshead displacement rates near 2.54×10^{-5} cm/s (10^{-5} in./s) or greater. For notched specimens, threshold stress intensities calculated at minimum displacement rates for both alloys at the -1.00 V polarization level correspond well with K_{th} values determined for compact DCB and cantilever beam type samples at similar polarization levels in seawater under dynamic straining conditions. Specifically, for notched AISI 4340 steel strained at 1.3×10^{-7} and -1.00 V versus SCE, a threshold stress intensity of 26.7 MPa-m^{0.5} (24.3 ksi in.^{0.5}) is determined. This value compares well with a 22 MPa-m^{0.5} (20 ksi in.^{0.5}) value obtained from cantilever beam testing [18], and underestimates a 40 ksi in.^{0.5} value obtained in a J-integral study [11]. For the 5Ni-Cr-Mo-V alloy, a notched stress-intensity value of 46.4 MPa-m^{0.5} (42.3 ksi in.^{0.5}) is obtained at a 5×10^{-7} displacement rate that compares well with a sustained plus cyclic loaded cantilever beam threshold value of 43.9 MPa-m^{0.5} (40 ksi in.^{0.5}) [18].

Slow Strain Rate Tests: Effect of Polarization Level

Figures 9 and 10 illustrate the influence of cathodic polarization level on ductility for smooth specimens tested at 3×10^{-7} /s. The reversible potential for the reduction of water, as indicated, is -0.74 V versus SCE. Hydrogen susceptibility is observed particularly when the polarization level is more negative than this potential for both alloys. The -0.90 to -1.00 volts versus SCE polarization range is typical of cathodic protection levels for steels in marine service [22,51,55,56]. The 5Ni-Cr-Mo-V steel alloy is more resistant to hydrogen assisted damage over this range of potential.



DISPLACEMENT RATE (in./sec)

FIG. 5—Relationship between displacement rate and ductility for tapered hourglass AISI 4340 steel specimens in ASTM artificial ocean water at -1.00 V versus SCE.



FIG. 6—Relationship between displacement rate and breaking load expressed as the percentage of maximum inert environment load for notched AISI 4340 steel in ASTM artificial ocean water at -1.00 V versus SCE.



FIG. 7—Relationship between displacement rate and ductility for tapered hourglass 5Ni-Cr-Mo-V steel specimens in ASTM artificial ocean water at -1.00 V versus SCE.



FIG. 8—Relationship between displacement rate and breaking load expressed as the percentage of maximum inert environment load for notched 5Ni-Cr-Mo-V steel in ASTM artificial ocean water at -1.00 V versus SCE.

Slow Strain Rate Tests: Effects of Preexposure Condition

Samples were precharged in order to differentiate strain enhanced absorption effects from time dependent diffusion in controlling the strain rate dependent hydrogen susceptibility observed in the slow strain rate tests (Figs. 3 to 8). These additional tests were conducted on smooth cylindrical specimens in ASTM artificial ocean water. These tests involved the following sequence: (1) exosure under freely corroding conditions to develop a slightly corroded surface (16 to 20 h), (2) 100 h cathodic polarization at -1.20 V versus SCE with no strain, and (3) straining to failure at -0.75 V versus SCE, a slight cathodic polarization level. One hundred hours at -1.2 V provided ample time for diffusion and internal hydrogen accumulation as shown previously [51]. The cathodic potential of -0.75 V versus SCE is negative of the reversible electrode potential for the reduction of water reaction in this electrolyte but affords only slight cathodic polarization and limited hydrogen damage when considered separately, as can be ascertained from Figs. 9 and 10.

Figures 11 and 12 illustrate the data from the preexposure experiments for the AISI 4340 steel and the 5Ni-Cr-Mo-V alloy, respectively. The solid line in Figs. 11 and 12 summarize the relationship between reduction in area and strain rate for -1.00 V versus SCE when cathodic polarization was conducted simultaneous to straining (Figs. 3 and 4). Note that no significant hydrogen susceptibility is indicated in any of the 100 h -1.20 V cathodic preexposure tests even at the two slower strain rates. Significant losses in ductility are observed in the case of -1.0 V polarization with concurrent straining and cathodic polarization (Figs. 3 and 4).

It is certain that some hydrogen enters the steel during the preexposure period at -1.2 V. However, it appears that an insufficient amount enters to promote hydrogen cracking susceptibility if there is insufficient straining concurrent with cathodic charging when there is a corrosion film prior to cathodic polarization.



FIG. 9—Relationship between cathodic polarization level and ductility for AISI 4340 steel in ASTM artificial ocean water at $3.0 \times 10^{-7} \text{ s}^{-1}$ strain rate.



FIG. 10—Relationship between cathodic polarization level and ductility for 5Ni-Cr-Mo-V steel in ASTM artificial ocean water at $3.0 \times 10^{-7} \text{ s}^{-1}$ strain rate.

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Hydrogen Permeation Experiments

Steady-State Hydrogen Permeation Measurements: Effect of Galvanostatic Cathodic Current Density and Surface Condition—Figures 13 and 14 show the relationship between galvanostatic charging current density and steady-state hydrogen permeation current density (at 100 h or greater charging time to assure steady state) for the AISI 4340 steel and the 5Ni-Cr-Mo-V alloy, respectively. Note the large permeation rates for the case of the ICP surface versus the surface cathodically polarized after slight corrosion. The surfaces on which corrosion by electrolyte contact under freely corroding conditions occurs show the lowest hydrogen permeation fluxes per unit surface area and therefore the lowest hydrogen absorption rates for both steels. Conversely the ICP surfaces, which simulate the film free surface of a sufficiently strained crack tip, show substantially greater hydrogen absorption per unit area.

Influence of Mechanical Strain on Permeation Rates

Steady-state hydrogen permeation results from straining Devanathan-Stachurski experiments are summarized in Table 2. Note the large increase in the steady-state permeation flux after both plastic straining and cyclic straining at $4.5 \times 10^{-6} \text{ s}^{-1}$ or $2 \times 10^{-6} \text{ s}^{-1}$. These increases could be eliminated by the removal of cathodic polarization and the return to freely corroding conditions in a reversible manner. The data shown in Table 2 correspond quantitatively with the permeation data previously shown [52]. Rupture of the corrosion film and exposure of bare metal by straining increases the permeation flux in a similar manner to that hypothesized by moving from the corroded condition to the ICP condition for the nonstrained surfaces. The lower permeation rate observed



FIG. 11—Relationship between pre-exposure condition and ductility for AISI 4340 steel in ASTM artificial oceal water at various strain rates.



FIG. 12—Relationship between pre-exposure condition and ductility for 5Ni-Cr-Mo-V steel in ASTM artificial ocean water at various strain rates.



FIG. 13—Relationship between cathodic charging current density and steady-state hydrogen permeation current density as a function of surface condition: AISI 4340 steel (a) 0.6M NaCl where solution formed films are avoided by utilizing the instantaneous cathodic polarization approach, (b) 0.6M NaCl after slight corrosion.



FIG. 14—Relationship between cathodic charging current density and steady-state hydrogen permeation current density as a function of surface condition: 5Ni-Cr-Mo-V steel (a) 0.6M NaCl where solution formed films are avoided by utilizing the instantaneous cathodic polarization approach, (b) 0.6M NaCl after slight corrosion.

at 1 to 2% plastic strain apparently reflects the composite nature of the surface with small bare areas and larger areas of remaining intact film. Cyclic strain appears to increase the amount of bare metal surface area over a given period of time. This was particularly true for the 5Ni-Cr-Mo-V steel alloy where the initial permeation rate after cyclic straining at $4.5 \times 10^{-7} \text{ s}^{-1}$ was $0.30 \,\mu\text{A/cm}^2$. At a cyclic strain rate of $2 \times 10^{-6} \text{ s}^{-1}$, the steady-state permeation current density increased from 0.59 to 0.81 $\mu\text{A/cm}^2$ over a period of nearly 100 h.

	Hydrogen Permeation Current Density During Mechanical Perturbation, $\mu A/cm^2$							
Alloy	No Load	Elastic Strain 80 to 95% of Yield Stress	Plastic Strain, 1 to 2%	Cyclic Strain, $4.5 \times 10^{-7} \text{ s}^{-1}$	Cyclic Strain, $2 \times 10^{-6} \text{ s}^{-1}$			
AISI 4340"	< 0.20	0.53	0.87	1.17				
5Ni-Cr-Mo-V ^b	< 0.10	< 0.10	0.24	0.32	0.81			

TABLE 2—Steady-state hydrogen permeation current densities for two high-strength steels in seawater $(-500 \ \mu A/cm^2 \ cathodic \ current \ density).$

" Minimum of three experiments averaged.

^b One experiment.

Influence of Mechanical Strain on Diffusivity

In order to unambiguously determine whether a measured increase in hydrogen permeation flux is a result of an increase in the diffusivity or an increase in hydrogen absorption, these parameters must be separated. Diffusivity is related to permeation rate through the following expression under the circumstances described [60]

$$J = D^* C / L \tag{1}$$

where

 $D = \text{diffusivity } (\text{cm}^2/\text{s}),$

C = mobile subsurface hydrogen concentration (mole/cm³),

L = sample thickness (cm), and

 $J = \text{permeability (mole/cm}^2 \text{ s}).$

By utilizing the permeation rise and transient decay method discussed by McBreen [61], diffusivities were calculated during straining permeation experiments. This approach was previously utilized to study AISI 4340 steel [52]. A diffusivity value of 4.5×10^{-7} cm²/s (average of two measurements) was obtained under no straining for the AISI 4340 steel alloy that is in good agreement with the literature [62]. A diffusivity of 4×10^{-7} cm²/s was utilized for the 5Ni-Cr-Mo-V alloy as determined by Berman [63]. For AISI 4340 steel, diffusivity values were found to decrease under straining conditions as a result of dynamic generation of dislocations that serve as hydrogen trapping sites at room temperature. A similar effect was found for the 5Ni-Cr-Mo-V alloy under cyclic straining conditions as shown in Table 3. An example of permeation rise and decay transient data under cyclic straining conditions is illustrated in Fig. 15. The diffusivity decreases to a small fraction (0.07) of the value obtained under no load. This fraction represents the average data for a total of four permeation rise and decay transients under cyclic straining divided by 4×10^{-7} cm²/s. For AISI 4340 steel the data shown is the ratio of the average of eight measurements under cyclic strain divided by 4.5×10^{-7} cm²/s. For the case of continuous plastic strain, this is the ratio of two plastic strain measurements to 4.5×10^{-7} cm²/s. Since the ratio is less than one in all cases, no long range enhanced diffusion of hydrogen is indicated by dislocation movement or the formation of dislocation arrays. In fact, these lower diffusivity values indicate hydrogen trapping.

		Ratio of Diffusiviti	es, $D_{\text{straining}}/D_{\text{no load}}$ () ^a	
Alloy	No Load	Plastic Deformation, $\dot{\epsilon} =$ $4.5 \times 10^{-7} \text{ s}^{-1}$	Cyclic Strain in Plastic Region, $\dot{\epsilon} =$ $4.5 \times 10^{-7} \text{ s}^{-1}$	Cyclic Strain in Plastic Region, $\dot{\epsilon} =$ $2 \times 10^{-6} \text{ s}^{-1}$	Diffusivity Data under Nonstrained Conditions, cm ² /s
AISI 4340	1.0	0.31	0.45		4.5×10^{-7}
5Ni-Cr-Mo-V	1.0	—		0.07	4.0×10^{-7}

 TABLE 3—Ratio of diffusivity values as a function of mechanical perturbation for two

 high-strength steels.

" — indicates dimensionless units.



FIG. 15—Straining permeation rise and decay transient behavior for 5Ni-Cr-Mo-V steel in 0.6M NaCl under cyclic strain.

These findings support the concept of strain enhanced hydrogen absorption since there is no increase in "apparent" diffusivity to account for the increase in permeation rates observed in straining experiments.

Results of Hydrogen Evolution Kinetics Studies

Figures 16 and 17 show cathodic overpotential versus applied current density from the long term steady-state permeation studies for the charging side of the Devanathan-Stachurski sample under the two conditions previously discussed, ICP and slight corrosion. This overpotential is determined with respect to the reversible electrode potential for the reduction of water reaction at the measured pH. Note that the slope of the overpotential versus applied current density behaviors are all approximately the same. In both cases, the Tafel slope, ranging from 0.120 to 0.170 V per decade of current, is independent of the surface condition. The exchange current density for the corroded surface is approximately a factor of four to six times greater than for the ICP case. These results show that it is more difficult to obtain a large hydrogen overpotential on the corroded steel surface with the presence of a corrosion film than on the bare steel surface.

Discussion

Slow Strain Rate Tests: Discussion

One explanation for the observed decrease in ductility at applied cathodic potential during slower straining is that the time required for sufficient hydrogen to enter the specimen, diffuse to, and segregate at susceptible sites is only reached in those tests conducted at 10^{-4} s⁻¹ or slower. However, this explanation seems to be in contradiction with the results



FIG. 16—Steady-state overpotential versus cathodic current density relationship for AISI 4340 steel in alkaline 0.6M NaCl under the surface conditions of Fig. 13 (each data point is an average of three experiments).



FIG. 17—Steady-state overpotential versus cathodic current density relationship for 5Ni-Cr-Mo-V steel in alkaline 0.6M NaCl under the surface conditions of Fig. 14.

of the slow strain rate test conducted at -0.75 V versus SCE after cathodic charging at -1.2 V for 100 h under no strain. Adequate time for diffusion was available under these conditions as previously calculated [51] yet limited damage was observed.

A second and more likely explanation for the strain rate effect is that hydrogen entry is enhanced by surface deformation during the slow strain rate test once a critical strain associated with either film rupture or plastic deformation is attained. Conversely, hydrogen absorption is lower in alkaline seawater after corrosion with no straining. Slow straining does provide greater time for diffusion of hydrogen to susceptible sites prior to attainment of ductile fracture stress levels, however, diffusion time is a necessary but not a sufficient condition in order for damage to be maximized. A prerequisite for concurrent strain and cathodic polarization seems to exist independent of time. Embrittlement at 10^{-4} s⁻¹ or at faster strain rates is observed only if sufficient hydrogen has previously entered and permeated to deleterious trapping sites within the specimen [51]. This explanation is supported by a calculation of the time required for diffusion so that the bulk average lattice hydrogen content approaches the subsurface hydrogen content for the smooth cylindrical samples [51]. Consequently, time for diffusion can not be concluded to be the sole cause of the strain rate dependency. Slow strain rate results are consistent with either a film rupture or plastic strain induced enhancement of hydrogen absorption followed by the necessity of adequate remaining time for hydrogen diffusion prior to attainment of ductile overload. This is supported by the empirical observation that the minimum K_{th} observed in sustained plus slow cyclic loaded tests approaches the ΔK threshold obtained in low cycle corrosion fatigue testing and is lower than the K_{th} obtained in sustained load tests [18]. In the slow cyclic tests bare metal production at the crack tip may occur during each cycle keeping the crack tip almost continuously bare. Under these circumstances hydrogen absorption is maximized for the given electrochemical conditions. Consistent with this reasoning is the work of Endo. Komai, and Fujimoto [20]. In their study, low-cycle fatigue crack growth rate is maximized a and threshold ΔK values are lowered when the cyclic waveform utilized provides a rapid ΔK increase followed by a hold or slow decrease in ΔK . The large initial ΔK provides adequate crack tip strains to produce bare metal early in the cycle yet allow time for hydrogen diffusion to the zone of metal in front of the crack tip.

Hydrogen Permeation and Reaction Kinetics Experiments: Discussion

Hydrogen absorption and subsequent permeation rates are enhanced when a surface is free of corrosion products or films formed on contact with the electrolyte. These observations support the argument that fresh metal surfaces created during mechanical perturbation cause enhanced hydrogen absorption. It remains to be determined why this is the case. It is warranted, therefore, to discuss the mechanism for the water reduction reaction, and the adsorption-absorption process for hydrogen in steel.

In alkaline solution, the hydrogen absorption process occurs as a result of the water reduction reaction. This reaction is followed by chemical recombination of hydrogen and evolution, or absorption. Numerous studies of the hydrogen evolution reaction on steel and iron in aqueous acid and alkaline solution indicate the reaction kinetics to follow either the coupled discharge chemical recombination mechanism [64, 65], or rate determining discharge followed by chemical desorption [66, 67]. The Tafel slopes determined in this investigation are consistent with either and are also consistent with the findings of Frankenthal's investigation of steel in 3.5% sodium chloride [68]. The following reaction sequence describes

this process

$$H_2O + e^- \stackrel{\kappa_1}{\underset{\kappa_{-1}}{\leftarrow}} H_{ads} + OH^-$$
 (2)

where K represents a reaction rate constant here, and in the following expressions. This reaction is typically followed by chemical desorption, with a small quantity of hydrogen adatoms becoming absorbed.

$$H_{ads} + H_{ads} \frac{K_2}{K_{-2}} H_2$$
(3)

$$H_{ads} \xrightarrow{K_{abs}} H_{abs}$$
(4)

The forward rate of the water reduction reaction is expressed by the following equation when reaction 2 is displaced from equilibrium to the right as a result of cathodic polarization

$$i = 2FK_1C_{\rm H_2O}(1 - \theta) \exp(-\beta\Delta\phi_e F/RT) \exp(-\beta\eta F/RT)$$
(5)

where

 θ = fractional surface coverage of hydrogen,

F = Faraday's constant,

R = gas constant,

T = temperature,

 $C_{\rm H_{2}O}$ = concentration of the reacting species,

 $\Delta \phi_e$ = potential gradient at equilibrium,

 β = symmetry factor, and the exchange current density, i_0 is $i_0 = 2Fk_1(1 - \theta)\exp(-\beta\Delta\phi_e F/RT)$.

Equation 5 can be simplified to

$$i = i_0 \exp(-\beta \eta F/RT) \tag{6}$$

where η is the overpotential. The hydrogen surface desorption and the hydrogen absorption reaction rates are described in terms of the following current densities

$$i_1 = 2FK_2 (\gamma \cdot \theta)^2 - 2Fk_{abs} \cdot \gamma \theta \tag{7}$$

and

$$i_2 = 2FK_{abs} \cdot \gamma \theta - 2FK_{des}C_H - 2FK_2 (\gamma \theta)^2$$
(8)

where

 γ = surface concentration of adsorbed hydrogen when θ = 1, or the surface concentration $[H_{ads}] = \gamma \theta$,

 i_2 = rate of hydrogen entry, and

 i_1 = rate of hydrogen evolution.

Also, $i_2 = 2FJ$ where J has been given in Eq 1 if steady-state conditions are met. For the case of the cathodic polarization of steel in alkaline chloride, two assumptions may be made, that $(1 - \theta) \approx 1$, and that i_1 is much greater than i_2 . These assumptions are valid because

the permeation current density was always only a small fraction (10% or less) of the galvanostatic cathodic charging current density in this study and previous studies have indicated a low surface coverage on iron and iron based alloys [69,70]. Under these conditions, the fractional surface coverage for hydrogen adatoms on steel is a function of the hydrogen overpotential as given by the following

$$\theta = \{i_0/2FK_2\}^{0.5} \exp\{-\beta\eta F/2RT\}$$
(9)

At dynamic steady state, the subsurface hydrogen concentration, C_H is

$$C_{H} = (K_{\rm abs}/K_{\rm des}) \cdot \gamma \theta \tag{10}$$

Where $C_H = L \cdot J/D$, the mobile hydrogen concentration, at steady state. Figures 16 and 17 show that the presence of a corroded metal surface, with its greater exchange current density, results in a decreased overpotential compared to a bare steel surface when polarized to a constant current. Equation 9 indicates that a 200 mV lower overpotential for the corroded steel surface results in a decreased hydrogen fractional surface coverage under conditions where all other terms are constant. Equation 10 shows that the quantity of absorbed mobile hydrogen depends strongly on θ which is increased with overpotential. However, for the corroded steel surface it is also noted that the exchange current density is larger by a factor of 4 to 6. Taking both of these factors into consideration when using Eq 9 while keeping β as a constant, a larger hydrogen surface coverage is produced on the bare steel surface. Here, we do not address the possibility of a decrease in the rate constant K_2 or increase in the rate constant K_{abs} after film rupture or under ICP surface conditions that would also contribute significantly to the absorption argument. Additionally, the surface created by film rupture and slip step emergence at a crack tip would produce a large transient increase in current density and overpotential that does not occur for the galvanostatically polarized surfaces in this study. In fact, Turnbull [71], and Burstein and Kearns [72] have shown that the scraping of filmed steel or iron surfaces under cathodic polarization in alkaline solutions caused a two order of magnitude increase in the recorded current transient for experiments conducted under potentiostatic control. This increase occurs at the bare surface. This current would be accompanied by a transient increase in overpotential of approximately 200 mV on those bare surfaces. An increase in overpotential of 240 mV increases θ by an order of magnitude if all other variables remain unchanged. Thus, the increase in permeation rates observed under mechanical strain can be accounted for by an increase in the surface coverage of adsorbed atomic hydrogen on bare metal surfaces.

Mechanical Straining

The following comments concern the enhanced permeation current densities observed after mechanical straining. The explanation put forth here concerns the rupture of a metastable corrosion product or partially reduced corrosion product layer on the metallic surface. An estimate of the strain required to rupture such a film, that is, the critical strain, is of significant practical interest, since it is only then that enhanced hydrogen entry may occur. Estimates of anodically formed film fracture strains range from 10^{-2} to 10^{-4} for a variety of alloys, including steel and iron [73–80]. Since the exact nature of the film is ill-defined, an estimate of 10^{-3} has been previously used and found to correlate, approximately, with slow strain rate results [51]. At a constant strain rate of 4.5×10^{-7} s⁻¹, a strain of 10^{-3} could be achieved within 1 h. This critical strain is consistent with the cyclic, constant displacement rate results (4.5×10^{-7} , 200 min/cycle, producing a strain increment of 2.7×10^{-3} per half

cycle) and, also, continuous straining results. A strain of 10^{-3} is achieved under elastic straining before the onset of plastic deformation, yet less enhancement of hydrogen permeation was observed in the elastic region and a percentage of that increase could be accounted for by an increase in solubility as a result of lattice expansion. Based upon the partial molar volume of hydrogen in iron and a stress equivalent to the yield stress, lattice dilatation would increase the hydrogen solubility and consequently the permeation rate by approximately 24%. Assuming a thick wall tube and triaxial stresses equal to twice the yield stress, the permeability could be increased by 50%. Therefore, this elastic contribution does not account for the total increase in permeation rate actually observed with straining. It is concluded that film rupture contributes to the permeation increase. One possible explanation for the increased permeation rates after long times is that continuous cyclic deformation in the plastic region is necessary in order to sufficiently increase the amount of bare metal surface area.

Comparison of the required breakthrough times to the total available time of straining is warranted to insure that changes occurring at the entry surface may be observed at the exit surfaces during the time of the experiment. One percent of strain requires more than 5 h at a 11.43×10^{-7} cm/s (4.5×10^{-7} in./s) displacement rate. This is enough time for the increased hydrogen concentration at the charging surface to effect the permeation current measured at the exit surface according to a permeation lag time calculation for the hollow sample [81].

Hydrogen Diffusion and Trapping

Modifications of the recorded permeation flux as a result of trap formation have been observed for hydrogen permeation through iron based alloys [40,45,82,83]. It is known [40,45] that during rapid straining the filling of newly created traps with hydrogen decreases the lattice hydrogen content. The net result is a transient permeation decrease measured at the exit surface. The calculated apparent diffusion coefficient can also be decreased [82]. For the case of slow dynamic straining, if the trap formation rate is slow then depletion of the lattice hydrogen content is minimized. Consequently, no transient decrease in the exit permeation flux would be observed as a result of lattice depletion although the apparent diffusivity can be lowered as a result of plastic straining. Frankel and Latanision [45] have utilized the dimensionless parameter $D/\dot{\epsilon}L^2$ to distinguish whether lattice depletion by dynamic trapping or adequate lattice refilling will dominate permeation-time transient behavior under straining. The $\dot{\epsilon}$ is the strain rate, L is the sample thickness, and D is diffusivity. Low values of this dimensionless parameter indicate a dominance of the trapping effect, while intermediate values indicate that the two effects (dynamic trapping and lattice refilling) tend to offset and cancel each other since they have opposite effects on the measured permeation rate. High values indicate adequate lattice refilling so that no permeation rate decrease is seen upon straining. This criterion will indicate whether or not a permeation decrease during straining from trapping will offset and mask an increase in the recorded permeation flux as a result of the increase in hydrogen absorption from film rupture. Table 4 summarizes the previous compilation [40,42,45] and the results of this study. The large value of the dimensionless parameter for the 4340 alloy in this study at $4.5 \times 10^{-7} \, \text{s}^{-1}$ indicates that this strain rate was slow enough to permit adequate lattice refilling. Consequently, dynamic trapping by newly created dislocations was not a dominant factor in the recorded permeation flux. Measured increases in the subsurface mobile hydrogen content at 4.5×10^{-7} s⁻¹ are not substantially masked by the offsetting effect of dynamic trapping. However, in a single experiment on AISI 4340 steel at a strain rate of 2×10^{-6} s⁻¹ a large decrease in the permeation flux was observed after plastic yield consistent with a low value of 26.7 for the

Material	$D/\dot{\epsilon}L^2$	Observation	Reference
4130 steel	105	slight trapping	Berkowitz
2.25Cr-1Mo steel	0.135 to 1.35	substantial trapping	Kurkela et al.
AISI 4340	158	no trapping	this study
AISI 4340	27	substantial trapping	this study
5Ni-Cr-Mo-V	70 to 141	slight trapping	this study

 TABLE 4—Correlation between observation of hydrogen trapping during permeation testing and diffusional parameter.

diffusional parameter. For the 5Ni-Cr-Mo-V alloy, lower values overall are obtained for the diffusional parameter. This may explain why lower straining permeation rates are obtained for this steel as listed in Table 2.

Concerning the role of dynamic dislocation trapping of hydrogen in increasing embrittlement susceptibility, no direct conclusions can be drawn from this study. It is clear that there is not long range dislocation transport of hydrogen. Short range dislocation transport, followed by dislocation pile ups at slip barriers, and deposition of hydrogen at such sites may still promote hydrogen embrittlement. This type of phenomenon may play a significant role in increasing hydrogen susceptibility in addition to the enhancement of hydrogen absorption at the surface.

Conclusions

Increased hydrogen assisted cracking susceptibility of a 5Ni-Cr-Mo-V alloy steel is observed in seawater under slow strain rate, sustained plus cyclic loading, or monotonic loading as compared to static loading. This is shown to be at least partially caused by enhanced hydrogen absorption at fresh metal surfaces created by the straining. The results obtained for this alloy are quite similar to those previously obtained for AISI 4340 steel. However, in both cases it is not an increase in the gross total surface area that accounts for this effect but a replacement of a fraction of the filmed surface area with bare surface area after film rupture; the bare area having better hydrogen absorption characteristics per unit area. For both alloys studied, prior corrosion has a strong role in controlling the kinetics of the hydrogen absorption process and the relationship between strain rate and hydrogen susceptibility is explained by a film rupture-enhanced hydrogen entry scenario. These findings provide explanation for the empirically observed strain dependency in slow strain rate tensile, compact (J-integral), and dead weight plus cyclically loaded plane strain cantilever beam specimens. The decrease in sustained load threshold stress intensities with sustained plus cyclic loading to a threshold stress intensity approaching the low cycle corrosion fatigue ΔK cracking threshold can be rationalized to occur when the bare surface production rate in the former test approaches that in the latter with all other conditions being equal. These findings indicate why sustained plus cyclic loading of steels in seawater creates a more severe environmental cracking condition than sustained loading typical of laboratory cantilever beam tests.

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DISCUSSION

Howard W. Pickering¹ (written discussion)—Is it, in the following way, experimentally possible to test your conclusion that plastic strain facilitates hydrogen uptake by rupture of the surface film? Do you use a strong cathodic polarization on the sample in order to reduce the surface film, and then apply plastic deformation?

J. R. Scully and P. J. Moran (authors' closure)—Although the suggested experiment has not been performed, we report in the paper the following: After obtaining an increased hydrogen permeation rate during plastic and cyclic straining, cathodic polarization was terminated, momentarily, to allow the sample to reach freely corroding conditions and then reapplied. The new permeation rates were similar to the "as corroded" condition (very low) even though the sample was still under load. Permeation rates only increased after a sufficient increment of strain was again made available concurrent to charging. This observation supports our conclusion that plastic strain facilitates hydrogen uptake by rupture of surface films.

In regard to the suggested experiment, there is some evidence that it is difficult to completely electrochemically reduce the corrosion films formed on iron in alkaline solutions, (Refs 47-50 of the paper) to produce the same surface as present before corrosion, or to produce a bare surface as created by plastic straining. This situation is further complicated by the presence of alloying additions such as chromium and nickel. Does the surface of the alloy become enriched in these elements during corrosion because of preferential dissolution of iron? Does any chromium become incorporated in the corrosion film making it difficult to completely reduce the film? These issues plague this experiment. In summary, we agree that much additional work is necessary in order to fully understand this phenomenon.

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Thermomechanical Treatments and Hydrogen Embrittlement of Ferritic Stainless Steels with Different Interstitial Contents

REFERENCE: Iyer, R. N., Hehemann, R. F., and Troiano, A. R., **"Thermomechanical Treatments and Hydrogen Embrittlement of Ferritic Stainless Steels with Different Interstitial Contents,"** *Environmentally Assisted Cracking: Science and Engineering, ASTM STP 1049,* **W. B. Lisagor, T. W. Crooker, and B. N. Leis, Eds., American Society for Testing and Materials, Philadelphia, 1990, pp. 30–41.**

ABSTRACT: Hydrogen embrittlement of 26Cr-1Mo ferritic stainless steels, with low and high concentrations of interstitial elements of carbon and nitrogen and with high-temperature annealing or prestraining treatments or both, was investigated. Tests involved cathodic charging of the specimens in sulfuric acid solution at room temperature, with simultaneous tensile loading using a uniaxial constant load fixture. The steel with high interstitial contents (26-1S) hydrogen embrittled intergranularly, when either heated to 1050°C and subsequently water quenched, or plastically prestrained by 5% elongation; but the low interstitial alloy (E-Brite) hydrogen embrittled transgranularly only when both of these treatments were given in this order. The cracks originated at the surface grain boundaries in 26-1S and at interior precipitate regions in E-Brite. Based on interrupted tests and fractography, the inferred hydrogen embrittlement mechanism has been stress-induced niobium hydride formation in E-Brite; whereas, this mechanism has been hydrogen trapping and absorption by nitrogen and faceted titanium of these alloys in boiling chloride solutions can be analyzed from these mechanisms and invoking potential drop concepts.

KEY WORDS: hydrogen embrittlement, stainless steels, thermomechanical treatments, ferritic stainless steels, interstitial elements, prestrain, hydrogen-assisted cracking, mechanism, grain boundaries, fracture, hydrogen charging, fatigue (materials), cracking, environmental effects

Ferritic stainless steels are found to be more prone to hydrogen embrittlement than austenitic stainless steels [1-3]; one of the main reasons for this is considered to be the higher diffusivity of hydrogen in ferritic (bcc) alloys. Mohr [2] investigated failure of ferritic stainless steels, having the base composition of 26Cr and 1Mo, by electrochemical hydrogen charging of samples under constant tensile load. He found that 26-1 alloy, with higher contents of interstitial elements, such as carbon and nitrogen, failed when prestrained or heat-treated to coarsen the grains, prior to hydrogen charging under load. However, E-Brite, with a lower interstitial content failed by hydrogen embrittlement only under a grain-coarsened and prestrained condition.

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			Ch	emical C	ompositi	ion, % b	y weight			
Alloy Designation	С	N	Cr	Мо	Ni	Cu	Ti	Cb	Mn	Si
E-Brite 26-1S	0.002 0.02	0.004 0.068	25.88 26ª	1.05 1ª	0.23 0.25	0.01 0.07	ь 0.49	0.12 0.003	0.08	0.22

TABLE 1—Chemical composition of the alloys.

^a Nominal composition.

^b Not analyzed.

This paper reports essential findings of a detailed investigation of failure characteristics of 26Cr-1Mo alloys subjected to various prior heat-treatments and prestraining operations, and hydrogen charged under load. Mechanisms for hydrogen embrittlement (HE) are also considered based on interactions of hydrogen, material, and stress-strain conditions.

Experimental Procedures

Materials and Preparation

Ferritic stainless steel sheets, with a base composition of 26Cr-1Mo but with different interstitial contents, were utilized. The chemical analysis of these alloys is presented in Table 1. Some of the specimens were grain coarsened by heating them at 1050° C for 1 h in an atmosphere of nitrogen, with water quenching. A few of the specimens were then prestrained to 5% elongation, in air. All the specimens were milled to gage lengths of 50 mm (2 in.) and widths of 3.2 mm (1/8 in.). The final preparation of the specimens involved sequential sanding with 240, 320, 400, and 600 grit papers, degreasing with acetone, washing with distilled water, and drying with methanol.

Test Procedures

Tensile strength, yield strength, and percent elongation were determined using the Instron testing machine at 0.05 cm/min; these properties are given in Table 2.

Treatment	Yield Strength (0.2% Offset), MPa	Tensile Strength, MPa	Elongation, %
	E	BRITE	
A^a	379	503	23
\mathbf{B}^{b}	507	593	24
\mathbf{C}^{c}	303	448	18
\mathbf{D}^d	414	517	11
		26-18	
А	379	524	26
В	483	621	28
D	421	538	12

TABLE 2-Mechanical properties (longitudinal) of 26Cr-1Mo alloys.

^{*a*} A = mill-annealed (as-received condition).

^b B = 5% elongation (prestrained).

 $^{\circ}$ C = heated for 1 h at 1050°C and water quenched.

 $^{d}\mathbf{D} = \mathbf{C} + \mathbf{B}.$
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Hydrogen charging experiments were performed, under tensile stress and ambient conditions, in a glass cylindrical cell containing a solution of 5% sulfuric acid and 2 g/L of arsenic trioxide acting as a promoter for hydrogen entry into the specimen. A cylindrical platinum counter electrode and a saturated calomel reference electrode connected through a salt bridge with Luggin capillary were utilized. Uniaxial loads corresponding to 90% of the 0.2% offset yield strength were applied to the specimen using a cantilever arrangement; the choice of this level of stress is based on the fact that dislocations become mobile, but bulk yielding does not occur and, moreover, these alloys can withstand this level of stress for years under pure mechanical loading conditions. Hydrogen charging was done galvanostatically at a current density of 100 mA/cm². Elongation versus time was monitored using a dial gage and an appropriately designed timing device. Load-elongation tests were carried out in an Instron testing machine at 0.05 cm/min. Tested specimens were metallographically examined with an optical microscope and fractographically examined with a scanning electron microscope (SEM).

Results

A specimen of the grain-coarsened E-Brite shows the elongation versus time behavior (Fig. 1) when stress hydrogen charged (that is, hydrogen charged under load), that is typical of creep behavior; thus, no hydrogen-assisted failure occurred in this condition. This is in agreement with the findings of Mohr et al. [2]. However, reduction in percent elongation was observed on specimens that were stress hydrogen charged for specific periods of time and subsequently pulled in the Instron tester (in air), as shown by percent elongation versus load measurements with the Instron tester (Fig. 2); in this figure, percent elongation versus load curve of uncharged specimens serves as a reference to estimate loss in ductility due to hydrogen charging. The curve for the charged specimen shows serrated yield behavior, similar to the Portevin-LeChatelier effect in low carbon steels [4].

When the grain-coarsened E-Brite specimens were prestrained, prior to stress hydrogen charging, they failed due to hydrogen embrittlement. Figure 3 depicts the elongation versus time behavior of such a specimen. It is easily seen that this is not a simple creep behavior,



FIG. 1—Creep curve during hydrogen charging of grain coarsened E-Brite, stressed to 90% of the yield strength.



FIG. 2—Instron testing (at 0.05 cm/min) of grain-coarsened E-Brite after interrupted stress hydrogen charging.

but reminiscent of discontinuous extensions (that are characteristic of hydrogen-assisted cracking) eventually leading to failure in a relatively short time of about $2\frac{1}{2}$ h, compared to that of the grain-coarsened specimen that did not fail in over 150 h of charging (Fig. 1). Therefore, E-Brite becomes susceptible to hydrogen-assisted failure only when it is both grain coarsened and prestrained; this observation corroborates previous findings [2]. The sequence of events leading to failure is illustrated in Fig. 4, that shows Instron testing of specimens after different periods of hydrogen charging under loads corresponding to 90%



FIG. 3—Creep curve during hydrogen charging of grain-coarsened and prestrained E-Brite, stressed to 90% of the yield strength.



FIG. 4—Instron testing (at 0.05 cm/min) of grain-coarsened and prestrained E-Brite after interrupted stress hydrogen charging.

of the yield strengths. Drastic reductions in ductility can be clearly identified, as charging is done for increasingly longer periods. Perhaps, the most important feature is that of a single but large drop in load just accompanying initial yielding in each of the cases.

In order to understand more clearly how and why these events are occurring, SEM micrographs were taken at various stages of cracking. A completely failed specimen (that is, a specimen that failed in situ during hydrogen charging under load) shows a number of individual cleavage events on the fractured contour (Fig. 5a) that is characteristic of hydrogen embrittlement. Figure 5b shows a magnified portion of Fig. 5a at the later stages of crack growth, when the stress intensity factor and hence the strain rate are much higher. Specimens pulled to failure in the Instron testing machine after specific periods of charging indicated probable embrittling sites. For example, in Fig. 6a, many isolated initiation sites are visible, whose features are observed in the grain-coarsened as well as the grain-coarsened and prestrained cases; therefore, relevant points are illustrated with one or both of these cases. Further analysis of fracture surfaces with SEM shows a magnified view of the sites (Fig. 6b), indicating previous positions of precipitate phases. These are clarified more in Fig. 6c, where in one of the initiation sites a fractured precipitate is also visible.

In contrast, the high interstitial alloy, 26-1S, hydrogen embrittled in just the prestrained condition and the fracture path is intergranular, as shown in Fig. 7a and more dinstinctly seen in the magnified central portion (Fig. 7b). Figure 8 depicts the origin of hydrogen embrittled cracking in 26-1S; the cracks are clearly seen to be intergranular, originating at the surface. Whereas, in E-Brite that has lower amounts of interstitials, no cracking was observed on the surface.

Discussion

In the absence of significant interstitial elements, as in the case of E-Brite, hydrogenassisted failure occurs by cleavage fracture and the cracking is initiated at subsurface regions. These sites are seen to constitute some sort of precipitates. In E-Brite, niobium (Nb) and



FIG. 5—The SEM fractographs of grain-coarsened and prestreined E-brite failed in situ during stress hydrogen charging.



FIG. 6—The SEM fractographs of E-Brite specimens pulled in the Instron testing machine after interrupting stress hydrogen charging: (a) grain-coarsened and prestrained (30-min charging), arrows show cleavage fracture events; (b) grain coarsened (75-h charging), arrows show embrittlement (initiation) sites; and (c) grain coarsened (120-h charging), arrows show embrittlement sites and also a fractured precipitate (vertical arrow).



FIG. 7—The SEM fractographs of prestrained 26-1S failed by stress hydrogen charging.



FIG. 8—Optical micrographs of the surface of grain-coarsened and prestrained 26-1S, stress hydrogen charged for 2 min.

carbon (C) go into solution when heated at 1050° C and remain in solution upon quenching. This can be rationalized from the Nb-C binary phase diagram [5]. There is ample literature that gives credence to stress-induced niobium hydride formation [6–8]. The fracture features in Fig. 5b are akin to features observed in niobium hydride fracture (Fig. 6d of Ref 7), especially the inverse strain rate effect, that is, the increase in ductility as the strain rate is increased. As noted in the preceding section, the strain rate keeps increasing at the later stages of crack growth and, therefore, transition from a cleavage fracture mode to a ductile mode seen in Fig. 5 is phenomenologically similar to niobium hydride cracking. This aspect is further reinforced by the observations in Fig. 6, especially the fractured precipitate seen in Fig. 6c.

The hydride formation just described is unlikely in 26-1S due to its high interstitial content, especially nitrogen that traps hydrogen [9] and more importantly due to the hydride formers, like titanium (Ti), being in the combined state as titanium carbo-nitrides. In fact, the stress concentration effect of faceted carbo-nitrides present near the grain boundaries and also impurity segregates, especially nitrogen traps, lead to absorption of hydrogen to grain boundaries. Consequently, the 26-1S alloy fails intergranularly.

The serrated load-elongation curve for the stress hydrogen-charged grain-coarsened E-Brite specimen can be considered to occur by sequential solute (hydrogen) pinning of dislocations, as the specimen is continuously strained in the Instron. However, it is fairly well established that solute-hydrogen pinning effects are significant only at low temperatures [10]. In the present investigation, the observed serrated yield drops and reduction in ductility can be explained on the basis of niobium hydride formation and subsequent fracture events when pulled in the Instron testing machine (in air), immediately following stress hydrogen charging. But when a larger initial dislocation density is present in the alloy, as in the

prestrained case, niobium hydride can be precipitated during stress hydrogen charging. This is reflected on the nature of load-elongation curve changing to a single large load drop at yield commencement, when pulled in the Instron testing machine, just after stress hydrogen charging. This phenomenon can be associated with the fracture of these hydrides in this specimen.

The effects of phosphorus (P) and sulfur (S) segregation to grain boundaries on enhancing HE are well known [11-14]. Findings in this investigation point to other critical factors in HE hitherto not considered. These are the large influence of interstitial elements and hydride formers that may be present only in very small concentrations (<1%) in the alloy. Also, this investigation has brought out the role of thermomechanical history presenting secondary effects of phase transformations, such as precipitation/hydride formation concurrent with hydrogen charging. The HE susceptibility and mechanisms have also been shown to be altered drastically, including the fracture mode changing from a purely intergranular to a transgranular cleavage, depending on interstitial contents.

It can be further emphasized, therefore, that even in non-hydride forming alloys such as stainless steels, the presence of small amounts of hydride formers (like Nb, Ti, etc.) in their uncombined state can induce HE in an otherwise immune alloy. Even if these elements (that serve as stabilizers to prevent sensitization in stainless steels) occur as compounds, such as nitrides or carbides, HE can still occur by a different mechanism. That is when excess of interstitial elements (such as nitrogen) trap hydrogen at defect phases like grain boundaries or carbides (like TiC) or both with facets and sharp corners (located near grain boundaries) that act as local stress raisers concentrating hydrogen. In short, the balance between HE susceptibility and immunity is very critical and quite sensitive to micro-constituents in the alloy. But it is interesting to note that in the absence of trapping elements and in the presence of potential hydride formers in the combined state as carbo-nitrides, where these carbo-nitrides are fairly rounded, the alloy can be immune to HE. This was the case of as-received E-Brite that did not hydrogen embrittle even when prestrained, since the major stabilizer, Nb, was in the combined state as NbC and fairly well rounded in shape.

Finally, the findings in this study can very well be applied to the problem of stress corrosion cracking (SCC) of these alloys in boiling chloride solutions, which has been seen to progress via a hydrogen embrittled region ahead of the crack [2]. Increased hydrogen permeability and delayed failure of austenitic and martensitic steels, under anodic polarization conditions existing in stress corrosion cracking have been observed [15,16]. It is also now well known that with increasing anodic potentials, hydrogen evolution can actually increase rather than cease inside cracks and crevices [17].

In order to understand how during anodic polarization conditions hydrogen evolution can occur or similarly SCC can progress by HE, probably the most important link is the concept of potential drops inside cracks, crevices, and pits [17–19] and these potential drops could be more than a volt negative to the applied anodic potential. Thus, once a crack is initiated, say, by a combination of anodic dissolution and passive film breakage due to applied stress, the crack tip could be under hydrogen charging conditions primarily as a consequence of a potential drop. Subsequent crack propagation can therefore proceed by an HE mechanism such as previously enumerated. Changes in the actual operating mechanism of SCC in these alloys as a result of variations in interstitial contents, heat-treatments, and prestraining operations can be better understood in this light. It should be noted, however, that HE is but one of the several ways by which SCC can propagate and a critical deciding parameter could be the magnitude of the potential drop. This theory is still in the developing stage; but it is a potentially powerful concept to provide an insight into inner workings of localized electrochemically assisted failures, in general.

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Conclusions

1. Hydrogen embrittlement in a ferritic stainless steel (26Cr-1Mo) was found to be significantly sensitive to small concentrations of interstitial elements, particularly nitrogen and also on the thermomechanical history. The high interstitial alloy (26-1S) failed by HE intergranularly. Whereas, the low interstitial alloy (E-Brite) failed by HE only in the graincoarsened and prestrained condition and transgranularly.

2. Origin of HE cracks in 26-1S were seen to be at the surface grain boundaries. In contrast, no surface HE cracks were observed in E-Brite. The HE cracks seemed to originate at some precipitate regions in the grain-coarsened and prestrained E-Brite.

3. Series of load-elongation testing in the Instron testing machine, following stress hydrogen charging to different periods of time, showed specific characteristics of serrated yield drops in the case of grain-coarsened E-Brite and a single, large yield drop in the case of grain-coarsened and prestrained E-Brite. The former behavior was associated with sequential hydride formation and fracture events during Instron testing. The latter behavior was associated with the fracture during Instron testing of hydrides formed in the stress hydrogen charging stage.

4. The HE mechanisms seem to be different in the two alloys. In 26-1S, the presence of faceted titanium carbonitrides with sharp corners near grain boundaries, and also the presence of hydrogen trapping segregates, such as nitrogen, concentrated hydrogen absorption at these boundaries. In E-Brite, these were absent; however, when hydride formers like Nb were present in the uncombined state with sufficient dislocation density, stress-induced hydride formation became probable.

5. Involvement of an HE process in SCC could be explained on the basis of the potential drop concept and HE mechanism considered here.

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Influence of Overload and Temperature on Stress Corrosion Crack Growth Behavior in a Low-Alloy Steel

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ABSTRACT: An investigation was carried out to examine the influence of temperature and overload plastic zone size on stress corrosion crack (SCC) growth behavior in a low-alloy steel. Compact tension specimens with TL orientation prepared from SAE 4140 steel in hardened and tempered condition were used. Two pertinent variable conditions were chosen: (1) cold deionized water at 23°C and (2) hot deionized water at 80°C. The specimens were precracked in fatigue and then overloaded to various extent (5, 10, 25, and 50%). The SCC behavior of these specimens was studied, keeping them submerged in hot and cold deionized water.

The results of the present investigation demonstrate that the incubation period for crack growth decreases with increasing initial stress intensity factor and increasing temperature. The incubation period for crack growth was found to increase as an exponential function of the overload plastic zone size. In overloaded specimens, once the crack growth initiated, the crack growth rate was observed to be much higher than in the non-overloaded specimens. The crack growth rate in Region I was found to increase with increasing initial stress intensity factor and temperature. The crack growth rate in Region II was also found to increase with temperature, but was independent of the stress intensity factor.

KEY WORDS: stress corrosion cracking, incubation period, plastic zone size, crack growth rate, temperature, residual stress and activation energy, fatigue (materials), cracking, environmental effects

Nomenclature

- a Crack length
- a_0 Initial crack length
- a_r Effective crack length
- A Constant as given by Eq 2
- A_1 Constant as given by Eq 3
- **B** Specimen thickness
- C Constant as given by Eq 4
- C_1 Constant as given by Eq 5
- C_2 Constant as given by Eq 6
- E Modulus of elasticity

F(a/w) Calibration function for stress intensity factor

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- G Crack extension force
- K Stress intensity factor
- K_i Initial stress intensity factor
- $K_{\rm lc}$ Plane strain fracture toughness
- K_{max} Maximum stress intensity level
 - P Load
 - R Gas constant
 - R_p Plastic zone size (radius)
 - V Displacement
 - t_s Time of crack growth as given by Eq 1
 - t_f Time for failure
 - t_{inc} Incubation period for growth of crack
 - W Specimen width
 - T Temperature in degrees kelvin
- ΔH Activation energy for crack growth
- $(da/dt)_{I}$ Crack growth rate in Region I
- $(da/dt)_{II}$ Crack growth rate in Region II
 - m_1 Constant
 - m₂ Constant

Stress corrosion cracking is a very serious phenomenon that can drastically reduce the life of structural components. Under combined actions of stress and corrosion, crack growth rate can accelerate and lead to the failure of structures or load-bearing components, often with catastrophic consequences.

In recent years, the linear elastic fracture mechanics parameters, stress intensity factor, has been found very useful in characterizing stress corrosion crack growth behavior [1-4]. Specifically, the stress intensity factor can be used to describe the crack tip stress strain field, and thus the mechanical driving force necessary for the growth of stress corrosion cracks.

There are three important parameters in stress corrosion cracking: (1) The incubation period (t_{inc}) , defined as the period necessary for the start of crack growth under sustained monotonic loading in a corrosive environment; (2) the crack growth rate da/dt, defined as the amount of crack extension per unit time; and (3) the critical stress intensity required for the onset of crack growth, K_{lscc} . This parameter (K_{lscc}) is commonly referred to as the stress corrosion cracking threshold and is considered to be a material property for a particular material-environment system. The ratio of K_{lscc} and K_{lc} can be used [5] to describe a material's increasing susceptibility to stress corrosion cracking. All three of these parameters have practical significance. Once the appropriate values of these parameters have been determined, they can be used for structural design to establish the critical combination of applied stress and defect size below which stress corrosion cracking will not occur for a given material-environment system.

The stress corrosion crack growth rate when plotted in terms of $\log da/dt$ versus K often shows three distinct regions [6], as shown in Fig. 1. In Region I, or the linear region, the crack growth rate increases with increase in stress intensity factor. In Region II, or the steady-state crack growth region, the crack growth rate is relatively independent of stress intensity factor, whereas in Region III, or the fast fracture region, the crack growth rate again accelerates with increase in K.

One possible way to improve the functional life of a structural component subjected to stress corrosion cracking will be to introduce an overload plastic zone size ahead of the crack tip. This will reduce the constraint at the crack tip and quite probably improve the



FIG. 1—A schematic representation of crack growth rate as a function stress intensity factor.

overall life of the structural components subjected to a stress corrosion cracking environment. It is well known [7-13] that application of overload reduces the crack growth rate in a cyclic loading situation or fatigue in ambient atmosphere. It is also well known that shot peening or shot blasting of smooth bar tension specimens introduces residual compressive stresses, which increases the functional life of materials in a stress corrosion cracking environment. However, the influence of overload plastic zone size on the stress corrosion crack growth behavior of precracked specimens has not been studied or established. Therefore, this aspect needs examination in detail.

Numerous variables [14-30] can significantly influence incubation period, as well as the stress corrosion crack growth rate. Among these, the influence of material strength, temperature, and initial stress intensity factor are very important from a practical point of view. However, a careful analysis of the existing literature [14-30] indicates that the influence of these parameters on stress corrosion crack growth rate, as well as on the incubation period for growth of cracks, has also not been established for low-alloy steels. Further investigation will be beneficial.

The primary objective of the present investigation was to examine the influence of overload

C = 0.40%	- 0.031%	Ni $\sim 0.17\%$	
Si = 0.33%	P = 0.025%	Cr = 1.12%	
$\mathbf{Mn} = 0.93\%$	Cu~=~0.020%	Mo = 0.18%	

TABLE 1—Chemical composition of the material in percent by weight.

plastic zone size on the incubation period as well as on the stress corrosion crack growth rate of low-alloy steel SAE 4140. This material is used extensively in many structural applications, and stress corrosion crack growth data for this material is very important and has practical significance. The secondary objective of this investigation was to characterize the influence of temperature and initial stress intensity factor on the incubation period and the stress corrosion crack growth rate in this material for hot and cold deionized water.

Experimental Procedure

Material

The material was available in the form of a hot-rolled plate with identifiable rolling direction. The chemical composition of the material and its mechanical properties in as-received and heat-treated conditions are reported in Tables 1 and 2, respectively.

Specimen Preparation

The 2(T) compact tension specimens with TL orientation were prepared following various recommendations of ASTM Test Method for Plane-Strain Fracture Toughness of Metallic Materials (E 399-83). The thickness of the specimens was kept at B = 6 mm. The initial aspect ratio was kept at a/W = 0.40. After fabrication, the specimens were austenitized at 840°C for 1 h and quenched in oil. The specimens were then tempered at 400°C for 1 h and then air-cooled to room temperature. After heat treatment, the specimens were ground on both surfaces, cleaned, and degreased in acetone. The mechanical properties of the material were determined by testing three tensile samples from each condition. The average values are reported in Table 2. The microstructure of the material in heat-treated condition was predominantly tempered martensite with lower bainite.

Testing

The specimens were fatigue precracked in a Schenk-Electro hydraulic test machine to produce a sharp crack front. The fatigue precracking of 3 mm was carried out under load control mode at room temperature and ambient atmosphere. The load ratio was kept at R = 0.10 and K at 15 MPa \sqrt{m} .

	Yield Strength, MPa	Ultimate Tensile Strength, MPa	Elongation, %	Reduction in Area, %	Hardness
Annealed Hardened	417	655	25.7	68.9	197 (BHN)
and tempered	1385	1464	10.06	64.5	$43 \pm 1 (R_c)$

TABLE 2—Mechanical properties of the material.

After fatigue precracking, the specimens were loaded to an initial K_i level of 28 MPa \sqrt{m} , keeping the specimens submerged in hot and cold deionized water contained in a transparent plastic container. For the hot water experiment, the temperature of the bath was maintained within $\pm 2^{\circ}$ C by a thermostat heater arrangement measured close to the crack tip.

The crack extension on the specimens were monitored by an optical traveling microscope. The incubation period for crack growth and crack growth rates were determined. To examine the influence of overload plastic zone size on stress corrosion growth behavior, the initially fatigue precracked specimens were overloaded to 5, 10, 15, 20, 25, and 50% higher than initial K_i level (that is, 28 MPa \sqrt{m}), respectively, and then unloaded. Crack growth rates and the incubation period for crack growth in these specimens were then measured, keeping them submerged in hot and in cold deionized water, after reloading them to $K_i = 28$ MPa \sqrt{m} . The influence of initial stress intensity level on the stress corrosion crack growth behavior of the material was examined by loading the fatigue precracked specimens to various levels of initial stress intensity factor, that is, $K_i = 27, 28, 33$, and 46 MPa \sqrt{m} . The influence of temperature on incubation period and stress corrosion crack growth rates was also examined.

The data were analyzed using a computer program. The crack length versus time was plotted and a 7° polynomial was fitted through these data points. The crack growth rates were determined by differential of these polynomials.

For the sake of discussion, some terms used in this paper will be defined here. The failure time (t_f) is defined as the total time for the failure of the specimen, including incubation period (from start of the experiment until final fracture). Crack growth period (t_s) is defined as the period for crack extensions; that is

$$t_g = t_f - t_{\rm inc} \tag{1}$$

Results and Discussion

Influence of Initial Stress Intensity Level on Stress Corrosion Crack Growth Behavior

Figure 2 shows the plot of crack length versus time for the non-overloaded specimens in cold and in hot deionized water environments. Figure 3 indicates the influence of initial stress intensity factor on incubation period for these specimens in hot and in cold deionized water. Table 3 indicates the effect of K_i on failure time. In Fig. 4, the effect of K_i on stress corrosion crack growth rates in cold and hot water is reported. The crack front was observed to be flat in all stress intensity ranges. In cold water, the crack growth occurred mostly by spurts and jumps. However, in hot water, the crack growth was observed to be gradual and continuous.

It is evident from Fig. 3 that the incubation period for the growth of a crack decreases as the K_i level increases at the same temperature. Also, from Table 3, it is observed that the failure time decreases with increase in K_i level in both cold and hot water. As shown in Fig. 4, the stress corrosion crack growth rate in Region I, $(da/dt)_i$, increases at the same crack length level with increase in stress intensity factor. The figure also shows that there are only two regions in the crack growth rate versus stress intensity plot in our specimens. Region I was very small compared to Region II. However, Region I was more predominant in a hot water environment compared to cold water. Region III was not observed in the present investigation.

As discussed later, the crack growth process was found to be by stress-assisted diffusion of hydrogen. The results of this investigation also indicate that a combination of stress and



FIG. 2-Effect of temperature on crack extension.

critical concentration of hydrogen is needed for crack initiation. The increase in K_i level apparently increases the stress-assisted diffusion of hydrogen in the crack tip region. This, in turn, decreases the incubation period at higher K_i levels.

Some studies on high strength steels [15,21,22] indicate a linear relationship between crack growth rate and stress intensity factor. This was also found to be true in several other materials, such as 4340 steel [31], maraging 350 steels [32], etc. However, in some titanium alloys and high-strength aluminum alloys and other alloy steels [33-36], it was observed that stress corrosion crack growth rate attains a constant value [Region II] and becomes independent of the stress intensity factor. A similar phenomenon was observed in the present investigation.

As evidenced in Fig. 3, the log of the incubation period decreases as a linear function of the initial stress intensity factor in both cold and hot water. The statistical analysis of test results show that one can express this relationship in the form

$$t_{\rm inc} = A \cdot e^{-mK_{\rm i}} \tag{2}$$

where A and m are temperature-dependent constants for a specific material-environment system. The values of A were found to be 40 986.6 and 3022 for cold and hot water, respectively, and m was 0.04.

The crack growth rate in Region I similarly is a power function of the initial K_i level and can be expressed in the form

$$\left(\frac{da}{dt}\right)_1 = A_1 \cdot (K_i)^{m_1} \tag{3}$$

where A_i and m_i are constants for a particular material-environment system.



FIG. 3—Effect of stress intensity factor on incubation period.

The reason for discontinuous crack growth in cold water is discussed subsequently. In conventional tempered martensitic structure, the precise mechanism of stress corrosion cracking is not yet completely understood [37-38]. However, the most widely held view is that it is a stress-controlled brittle phenomenon caused by the presence of dissolved hydrogen in the region of stress concentration ahead of the crack tip. This view is also supported by the present experimental test results, where the formation of isolated microcracks ahead of

Stress Intensity Easter	Failure Time t_f , min			
$MPa\sqrt{m}$	Cold Water, 23°C	Hot Water, 80°C		
27.5	625	84.5		
28.6	608.86	82.50		
33.0	393	73.40		
46.2	244	63.40		

TABLE 3—Effect of initial stress intensity factor on failure time.



FIG. 4-Effect of stress intensity factor on crack growth rate.

the main crack tip in a cold water environment was observed. The fractographic examination of the fracture surfaces revealed the presense of intergrandular separation [47]. This is the usual mode for hydrogen assisted fracture. Moreover, activation energy measurement shows that diffusion of hydrogen in the crack tip region causes the crack growth. In order to permit crack advance, a certain critical stress must be achieved over some microstructurally significant distance ahead of the crack tip. This value of the critical fracture stress depends upon the microstructure of the steel and the local concentration of dissolved hydrogen. The concentration of dissolved hydrogen, on the other hand would depend on several factors [39-43], such as activity of hydrogen, permeability of steel, the magnitude of stress intensity, and the distance of microcrack initiation site ahead of the main crack tip.

At high stress intensities, the region of stress intensification ahead of the crack tip is extensive and the conditions necessary for the nucleation of microcracks can be satisfied at low hydrogen concentrations. Under these conditions, microcracks can develop in isolated regions ahead of the main crack. As a consequence of microcrack development and high stress intensity, there is localized tearing of intervening ligaments between microcracks, which then join with the main crack. Thus, crack growth occurs in a discontinuous manner in cold water. This is supported by the fact that the presence of tearing was observed at high K_i level [47] in cold water environment. In hot water, since the diffusion rate is higher, the hydrogen embrittlement region is far more extensive, thus making the crack growth more or less continuous.

At lower stress intensity ranges, it becomes more difficult to satisfy both the critical stress requirement for the nucleation of microcracks and the local strain requirement to cause rupture of the remaining ligament. As a consequence, the crack growth rate decreases with decrease in stress intensity range, which was found to be true in the present experimental work.



FIG. 5-Effect of temperature on incubation period.

Effect of Temperature on Stress Corrosion Crack Growth Behavior

The effect of temperature on incubation period for crack growth in these specimens is reported in Fig. 5. In Table 4, the effect of temperature on failure time, t_t , is reported.

It is evident from Fig. 5 that the incubation period at the same K_i level decreases with increase in temperature. The crack growth rate in Region I increases with increasing temperature, as shown in Fig. 4. The crack growth rate in Region II also increases with temperature (Fig. 6). The failure time decreases with increases in temperature, as shown in

Temperature, °C	t_f , min
23	608.85
40	187.29
60	86.85
80	73.40

TABLE 4—Effect of temperature on failure time, $K_i = 28.6 MPa\sqrt{m}$.



FIG. 6—A plot of log (da/dt)₁₁ against inverse of temperature.

Table 4. The incubation period was found to decrease as an exponential function of temperature; this can be expressed as

$$t_{\rm inc} = C \cdot e^{-m_2 \cdot T} \tag{4}$$

where C and m_2 are temperature-dependent constants.

The existence of Region II, or rate-limiting crack growth, was observed at all test temperatures in the present investigation. This observation is physically significant because it suggests that crack growth in Region II is controlled by some rate-limiting process, and is in agreement with the results of Williams [21].

In Fig. 6, the log $(da/dt)_{II}$ is plotted against the inverse of temperature in degrees kelvin. It is apparent that a straight-line relationship exists, and that the slope of the line gives a measure of activation energy for the steady-state crack growth process. For this materialenvironment system, the activation energy appears to be $\Delta H = 5700$ cal/mol/K.

Based on these observations, it is apparent that the steady-state crack growth is a thermally activated process and can be expressed as

$$(da/dt)_{\rm H} = C_1 \cdot e^{-\Delta H/RT} \tag{5}$$

where C_1 is the material constant and R is the gas constant.

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It has been pointed out [28] that the apparent activation energy for diffusion of hydrogen in iron and steel at temperatures below 473 K is in the range of 5000 to 6000 cal/mol/K. This value agrees well with the results of this investigation, indicating that in Region II the crack growth process is controlled primarily by hydrogen diffusion. At higher temperatures, the fracture surface was characterized by a brittle appearance with intergranular facets [44], thus also indicating that hydrogen diffusion in steel plays an important role in crack growth. Since diffusion is a temperature dependent process, higher temperature diffusion rate will be higher, thus increasing the crack growth rate in Region II. On the other hand, it is not surprising that the stress corrosion crack growth rate in Region I also accelerates with increasing temperature. The fact that $(da/dt)_1$ depends on the initial stress intensity factor, as well as on temperature, suggests that the crack growth process in Region I is also accelerated by hydrogen diffusion at the crack tip region. However, the activation energy for Region I crack growth rate was found to be less than the ΔH value obtained from Fig. 6. This means that in Region I the crack growth rate is controlled not only by hydrogen diffusion, but by some other mechanism that occurs concurrently. This mechanism has not been identified yet. Further studies are necessary to resolve this issue.

At higher temperatures, stress-assisted diffusion of hydrogen at the crack tip region increases, causing a large accumulation of hydrogen in a relatively shorter period of time. Consequently, nucleation of microcracks will be easier, leading to a lower incubation period. This also increases the crack propagation rate, making the crack growth gradual and continuous.

An analysis of the existing literature indicates that very few [6,33,34] studies have been carried out to examine the influence of temperature on stress corrosion crack growth behavior. Some studies by other workers [6,26] also indicate that the stress corrosion crack growth process is a thermally-activated process and increases with temperature, similar to the present test results. On the other hand, other workers [27] observed no significant effect of temperature on stress corrosion crack growth rate in a nickel-chromium-molybdenum (Ni-Cr-Mo) steel. This difference in the influence of temperature on stress corrosion crack growth behavior is probably related to the fact that the micromechanism of crack growth at high temperatures can be different for different materials, depending upon the susceptibility of microstructure for environmental reaction, and the solubility of hydrogen in the microstructure.

Influence of Plasticity on Stress Corrosion Crack Growth Behavior

The influence of overload plastic zone size on incubation period for growth of cracks in hot and in cold deionized water is reported in Fig. 7. In Figs. 8 and 9, the crack growth rate in hot and cold water is plotted as a function of overload plastic zone size. The plastic zone size was calculated using McClintock and Irwin's [45] equation, and plane stress condition was assumed to exist because of low B/W ratio in our specimens. It is apparent that as the overload plastic zone size increases, the incubation period increases in both hot and cold water. This increase is more significant for overloads of 25% or higher. The crack growth process was observed to be discontinuous in overloaded specimens in cold water, but was continuous in a hot water environment. In Fig. 10, the crack growth rate in Region II is plotted against overload plastic zone size. It is apparent that crack growth rate in Region II decreases with increase in overload plastic zone size.

Table 5 reports the effect of overload plastic zone size on the time of failure of cold and hot deionized water. It is apparent that the total time of failure remains more or less constant until after 25% overload. However, once crack growth was initiated, the growth rate for cracks in the rest of the specimen was found to increase with increased periods of exposure, that is, t_g is lower in cold water as percent overload increases (Table 6). Also, plot of log



FIG. 7-Effect of overload plastic zone size on incubation period.

time versus plastic zone size gives a straight-line relationship, as shown in Fig. 7, indicating that the incubation period increases as an exponential function of overload plastic zone size. Based on this result, one can express the incubation period as

$$t_{\rm inc} = C_2 \cdot e^{m_3 \cdot R_p} \tag{6}$$

where m_3 and C_2 are temperature-dependent material constants. In Fig. 11, log $(da/dt)_{II}$ is plotted against the inverse of temperature for overloaded specimens. The activation energy obtained from this figure was found to be 3370 cal/mol/K. This value is lower than the value obtained from Fig. 6. This indicates that, in overloaded specimens, the crack growth process has been altered and supports the fact that crack growth rate in Region II indeed is higher in overloaded specimens.

Thus in the present investigation, a significant reduction in t_s in cold deionized water was observed when the specimen was overloaded, compared to a non-overloaded specimen. The incubation periods for these overloaded specimens were significantly higher than for non-



FIG. 8-Effect of overload on crack growth rate.







FIG. 10--Effect of overload plastic zone size on Region II crack growth rate.

overloaded specimens. However, once a crack was initiated, the crack growth rate in the rest of the specimen was higher than in the non-overloaded specimens. This higher incubation period in overclouded specimens compared to non-overloaded specimens, appears to be due to the fact that overload produces compressive residual stresses in the crack-tip region. This in turn would cause a reduction in mechanical driving force. Hence a significant increase in incubation period is produced in overloaded specimens because longer time intervals are recognized for initial concentrating hydrogen. However, once a crack is initiated, the crack

		Failure Time, s	
Overload, %	Cold Water ^a	Hot Water ^a	Hot Water ^b
0	36 530	4 404	5 070
5	31 230	4 973	
10	29 160	4 573	6 135
25	32 788	6 924	12 978
50	356 740	86 691	

TABLE 5-Effect of overload on failure time.

^a $K_i = 28.6 \text{ MPa}\sqrt{\text{m}}.$

^b $K_i = 27.5 \text{ MPa}\sqrt{\text{m}}.$



FIG. 11—A plot of log $(da/dt)_{ii}$ against inverse of temperature for 25% overloaded specimens.

growth rate is much higher, due to the larger contribution of the hydrogen embrittlement regions in the specimens. This was also supported by the fact that t_g was also lower in cold water for 50% overloaded specimens where the specimens were exposed to a longer period than in hot water for similarly overloaded specimens. In overloaded precracked specimens, compressive stresses [12,13] exist in the plastic zone region. The presence of these compressive stresses tends to increase the incubation period by the mechanism discussed pre-

	t_{g} , min			
Overload, %	Cold Water ^a	Hot Water"	Hot Water ^b	
0	288.85	61.07	64.5	
5	205,50	72.77		
10	160.00	63.21	72.10	
15		59.67	70.35	
20		•••	63.56	
25	136.5	99.00	67.05	
50	65.68	74.81		

TABLE 6-Effect of overload on t.

 ${}^{a}K_{i} = 28.6 \text{ MPa}\sqrt{\text{m}}.$ ${}^{b}K_{i} = 27.5 \text{ MPa}\sqrt{\text{m}}.$

viously. The presence of residual stresses apparently lowers [46] the activation energy for crack growth. Moreover, compromise stress can produce stress induced martensites in the crack tip region which are more susceptible for hydrogen embrittlement. As a result crack growth rate increases in the rest of the specimens. Furthermore, compromise stresses can generate dislocation [37] which can assist the diffusion of hydrogen in the crack-tip region. This would contribute to higher crack growth rate.

Conclusions

1. The incubation period for growth of cracks in both hot and cold deionized water increases with an increase in overload plastic zone size.

2. The incubation period decreases with increasing temperature and initial stress intensity factor.

3. The stress corrosion crack growth rate in Region I in SAE 4140 steel in deionized water increases with increase in temperature and initial stress intensity level.

4. The Region II crack growth was found to be a thermally-activated process, and increases with temperature.

5. The incubation period for growth of the crack can be expressed as

$$t_{\rm inc} = C_2 \cdot e^{m_3 R_p}$$

where C_2 and m_3 are temperature-dependent constants.

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Role of the Oxide Film in the Transgranular Stress Corrosion Cracking of Copper

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ABSTRACT: Cyclic voltammetry, ellipsometry, and slow strain rate tests have been carried out on copper monocrystals in 0.1 M sodium acetate and 1 M sodium nitrite. These studies demonstrate that the presence of an oxide film is necessary but not sufficient to induce transgranular stress corrosion cracking, and that the growth rate and other characteristics of the oxide(s) are important factors. The results are discussed in terms of the film-induced cleavage model for cracking.

KEY WORDS: cracking, environmental effects, copper, stress corrosion cracking, nitrite, acetate, oxide, ellipsometry, voltammetry

Even though both types of stress corrosion cracking (SCC) occur in many systems, the intergranular (I) and transgranular (T) forms are believed to occur by basically different mechanisms. The mechanism of I-SCC is generally agreed to involve a slip dissolution process, but that of T-SCC remains controversial. There is strong evidence that T-SCC propagates by discontinuous brittle fracture [1], but the cause of the embrittlement remains obscure. Several candidates have been put forward, including hydrogen embrittlement and adsorption, but the present paper focuses on a more recent concept, film-induced cleavage [2]. This model, proposed by Sieradzki et al. [3,4], postulates that brittle fracture results from the formation of a coherent film at the crack tip. Under the applied tensile stress, the lattice misfit between the film and the substrate generates stresses that may, provided that the film has certain properties, trigger a brittle crack in the film that then propagates through the unaffected ductile substrate. The film was initially thought to be a dealloyed layer but the observation [3-6] that pure copper undergoes T-SCC in aqueous sodium nitrite (NaNO₂) ruled out selective dissolution as an exclusive cause of failure. Copper forms an oxide film in the nitrite solution, and therefore it was suggested that such films can also induce cracking [3]. Sieradzki et al. [7] suggested that the film needs to reach a critical thickness in order to trigger a brittle crack, and that parameters such as the magnitude of the epitaxial stresses, the nature and mechanical properties are also relevant.

The failure of copper presents an opportunity to conduct a systematic study of the role

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of the oxide since both dealloying and, on thermodynamic grounds, hydrogen embrittlement can be ruled out as contributing factors. The primary objective of the present study was to determine if the presence of the oxide film is necessary to induce T-SCC in copper. This was accomplished by carrying out slow strain rate tests in the presence and absence of an oxide film, determined by cyclic voltammetry and ellipsometry.

Aqueous 1 M NaNO₂ was the initial choice for this study. However, this solution is unstable at low pH, forming HNO₂ and decomposing according to

$$3 \text{ HNO}_2 = \text{H}_3\text{O}^+ + \text{NO}_3^- + 2 \text{ NO}$$

The bulk of the experiments were then conducted in aqueous sodium acetate (NaAc). This buffer solution was chosen because it is known to form a uniform cuprous oxide film on copper [8], and to cause T-SCC in brass [9]. It will be seen that this solution also causes T-SCC in copper.

The second objective of this work was to determine the growth kinetics of the oxide and some of its characteristics, and to correlate these with susceptibility to T-SCC. For this purpose, tests were carried out in 0.1 M NaAc, pH 5.5, and 1 M NaNO₂, pH 9.

Experimental

The oxides of copper are unstable at low pH [10], thus it is possible to test the T-SCC susceptibility of copper in the pH range where the oxide is stable and in the range where it is unstable. A 0.1 *M* NaAc solution was used to conduct slow strain rate tests on copper monocrystals at basic (pH 10), near neutral (pH 5.5) and acidic pH (pH 3) at several applied anodic and cathodic potentials. Strain rates between 10^{-7} s⁻¹ and 8.10^{-5} s⁻¹ were used. Time to failure, maximum engineering stress (UTS), and elongation to failure were recorded; the nominal crack velocity was calculated by dividing the length of the longest crack measured on the fracture surface or along the specimen gage length by the total time to failure. Note that the nominal crack velocity, as defined here, underestimates the crack growth rate as it includes initiation as well as propagation.

Most tests were performed on copper monocrystals (99.99% by weight) of random orientation grown from the melt in the shape of tensile specimens, but several involved crystals with the tensile axis about 10° from the $\langle 110 \rangle$ axis, the wider side face of their rectangular cross section being parallel to the $\{110\}$ plane. The latter were sliced from a 40-mm-long rod, 12.5 mm in diameter. The specimens had a 25 by 3 by 1.5 mm gage length. They were first mechanically polished to 600 grit and then electropolished with a 50% by weight phosphoric acid containing dissolved copper. The cleaning procedure was the same as already reported [11]. The gage sections and fracture surfaces of the specimens were observed using optical and scanning electron microscopy (SEM).

Slow potentiodynamic polarization curves were first carried out on randomly oriented monocrystals in 0.1 *M* NaAc at three pH values and in 1 *M* NaNO₂ but more information was obtained by conducting cyclic voltammetry on {110} faces at a scan rate of 20 mV/s in 0.1 *M* NaAc, pH 3 and 5.5, and 1 *M* NaNO₂, pH 9, and only these will be reported here. The samples used for the voltammetry were mounted in epoxy with an exposed surface area of 4.2 cm². Usually, ten scans were run in each experiment and the voltammograms that are presented correspond to the tenth scan in all cases. Sample preparation was the same as just described except that mechanical polishing was carried out to 1 μ m diamond prior to electropolishing. The counter electrode was graphite for the polarization curves and platinum for the voltammetry.

Ellipsometry was performed on the same {110} oriented samples used for cyclic voltam-

metry. An automatic ellipsometer was used to null the intensity of a monochromatic green light beam ($\lambda = 5461$ Å) generated by a mercury source. The details of the technique used for corrosion studies have been described elsewhere [12,13]. After introduction of the solution, the sample was cathodically polarized to reduce any air-formed oxide, the change in analyzer angle (A) and polarizer angle (P) being monitored until they were constant. The potential was then stepped to the desired value, the variation of P and A being recorded every 5 s up to 1000 s and then every 300 s until both parameters did not change significantly, usually up to at least 3000 s. Measurements were carried out at different applied potentials in 0.1 M NaAc of pH 3 and 5.5 and 1 M NaNO₂ of pH 9. The change in ellipticity of the light upon reflection is usually measured in terms of the two parameters, Δ and Ψ , that respectively represent the relative change in phase and in amplitude of the two electrical field vectors parallel and normal to the plane of incidence. Computation of the values of Δ and Ψ and film thicknesses were carried out using a Fortran program developed by Mc-Crackin [14]. After the tests, samples were observed with an optical microscope to compare the appearance of the oxide under the different electrochemical conditions.

For all three kinds of experiments, the solution pH was adjusted just before the tests using glacial acetic acid or sodium hydroxide in 0.1 M NaAc, and sodium hydroxide in 1 M NaNO₂. It was also measured at the end of the tests. The reference electrode was a saturated calomel electrode in all cases, and all potentials are referred to the saturated calomel electrode (SCE).

Results

Voltammetry

Figure 1 displays the behavior of copper in 0.1 *M* NaAc at pH 3 and 5.5. At the latter pH, an oxidation peak and a corresponding reduction peak are observed at +0.02 and -0.08 V, respectively. Such peaks have previously been interpreted as the formation and reduction of oxides on copper in alkaline and weakly acidic solutions [15-27]. The values of these peak potentials are close to the Cu/Cu₂O equilibrium potential of -0.096 V. Note that the current continues to increase after the anodic peak, behavior that is consistent with active dissolution or the formation of a second oxide, or both, in this case CuO. The gradual decrease of the reduction peak with decreasing potential suggests the occurrence of a diffusion limited process probably associated in this case with the reduction of dissolved copper species. No oxidation and reduction peaks are observed at pH 3, indicating the absence of oxide(s). The arrows delineate the range of potentials used for the slow strain rate tests that will be presented in Table 1.

Figure 2 displays the behavior of copper in 1 M NaNO₂, pH 9. In this case, well-defined oxidation peaks are observed at -0.32 and -0.035 V, with corresponding reduction peaks at -0.6 and -0.23 V. These values are consistent with the formation of Cu₂O and CuO. The same experiment on platinum did not show any peaks in this range of potentials, eliminating the possibility that these peaks in copper are associated with reactions of the nitrite. As in Fig. 1, the arrows indicate the range of potentials used for the slow strain rate tests in 1 M NaNO₂, pH 9, Table 2.

Figure 3 compares the behavior of copper in $1 M \text{NaNO}_2$, pH 9, and in 0.1 M NaAc, pH 5.5. The much larger currents in 0.1 M NaAc are evident. The decrease of the reduction peak current extends over a wider range of potentials than in Fig. 1, due probably to larger concentrations of dissolved species because of the more noble potential at which the sweep was reversed. The appearance of a second cathodic peak very close to the first suggests that some CuO may have formed. The lower currents and the much more well-defined peaks in



FIG. 1—Steady-state voltammograms of $\{110\}$ copper surfaces in 0.1 M sodium acetate (sweep rate is 20 mV/s). The arrows indicate the range of potentials used for the slow strain rate tests.

рН	Potential, ^a V SCE	Strain Rate/s	UTS, ksi (MPa)	Elongation to Failure, %	Nominal Crack Velocity, m/s	Mode of Failure
				AIR		
		$1 \cdot 10^{-6}$	18.5(127.7)	35.2		ductile
			Ox	ide Film		
10.3	0.11	$1 \cdot 10^{-6}$	13.2(91.1)	15.5	1.6 10-9	T-SCC
5.5 ^b 5.5 ^b 5.5 ^b	0.05 0.05 0.05	$\begin{array}{r} 8 \cdot 10^{-6} \\ 5 \cdot 10^{-6} \\ 1 \cdot 10^{-7} \end{array}$	15(103.5) 13.7(94.5) 8.5(58.7)	53.2 38.5 8	5.6 10 ⁻¹⁰ 4.6 10 ⁻¹⁰	ductile ductile + T-SCC T-SCC
5.5 5.5 5.5 5.5	$0.11 \\ 0.08 \\ 0.04 \\ 0$	$1 \cdot 10^{-6} \\ 1 \cdot 10^{-6} \\ 1 \cdot 10^{-6} \\ 1 \cdot 10^{-6} \\ 1 \cdot 10^{-6}$	10.2(70.4) 13.5(93.1) 21.6(149)	13 32 35	$\begin{array}{c} 2 \ 10^{-9} \\ 5 \ 10^{-10} \\ 4.7 \ 10^{-10} \\ 2.5 \ 10^{-10} \end{array}$	T-SCC T-SCC T-SCC ductile + T-SCC
			N	O OXIDE		
3 3 3 3 3	$\begin{array}{c} 0.05 \\ 0.01 \\ - 0.06 \\ - 0.03 \\ - 0.06 \end{array}$	$\begin{array}{r} 1 \cdot 10^{-6} \\ 1 \cdot 10^{-6} \\ 1 \cdot 10^{-6} \\ 5 \cdot 10^{-6} \\ 5 \cdot 10^{-6} \end{array}$	17(117.3) 14.3(98.7) 23(158.7) 15.9(109.7) 15.4(106.3)	25 35 37 44 37	 	ductile ductile ductile ductile ductile ductile

TABLE 1—Results of slow strain rate tests on copper monocrystals in 0.1 M sodium acetate.

^{*a*} The corrosion potential for pH 3, 5.5, and 10.3 were respectively -0.04, -0.06, and -0.03 V SCE (saturated calomel electrode) before the tests.

^b Oriented crystals; the remainder are randomly oriented.



FIG. 2—Steady state voltammograms of $\{110\}$ copper surfaces in 1 M sodium nitrite, pH 9, (sweep rate is 20 mV/s). The arrows indicate the range of potentials used for the slow strain rate tests.

1 *M* NaNO₂ strongly suggest more stable oxides and little or no dissolved species. The mechanism of formation of the oxides in this alkaline solution may involve dissolution and reprecipitation [21,28,29] or solid-state growth [18,25,26]. A duplex structure is likely, as suggested by previous work [16,18-21,25-27,30,31].

Ellipsometry

0.1 M Sodium Acetate—Ellipsometric studies were conducted in 0.1 M NaAc, pH 5.5, in the potential range where the voltammetric data, Fig. 1, indicated the presence of an oxide, namely, above 0 V. Figure 4 illustrates the relative phase change, Δ , with time at 0 V.

Potential, V SCE	Nominal Crack Velocity, m/s			
	Present Work (Monocrystals Strain Rate = 10 ⁻⁶ s ⁻¹)	Yu and Parkins [34] (Polycrystals Strain Rate = $1.8 \cdot 10^{-6} \text{ s}^{-1}$)		
0.2		1.2 · 10-8		
0.1		$1.2 \cdot 10^{-8}$		
0.05	3.3 · 10 ⁻⁹	$1 \cdot 10^{-8}$		
0	$1.9 \cdot 10^{-9}$	9 · 10 ⁻⁹		
-0.05		2.5 - 10-9		
Ecor				
(-0.07)	$1.3 \cdot 10^{-9}$			
-0.1		$4.5 \cdot 10^{-10}$		
-0.15	0			

TABLE 2—Nominal transgranular crack velocities for copper tested under slow strain rate in 1 M sodium nitrite, pH 9.



FIG. 3—Comparison of steady-state voltammograms of $\{110\}$ copper surfaces in 0.1 M sodium acetate, pH 5.5, and 1 M sodium nitrite, pH 9 (sweep rate is 20 mV/s).

Essentially, Δ is inversely related to film thickness and the data confirm that a film is growing. Data for pH 3 at 0 V are also presented in Fig. 4; the fact that Δ remains constant with time confirms the conclusion of the voltammetry, Fig. 1, that no oxide is present. Similar results were obtained at anodic potentials of +0.01 and +0.05 V.

Insight into the mechanism of oxide growth can be obtained from the simultaneous time variation of Δ and the relative amplitude change, Ψ , the latter being related to the optical properties of the surface [32]. Figure 5a illustrates data for pH 5.5, at +0.05 V. A detailed interpretation of these curves is beyond the scope of this paper, but it is relevant to note that the inflections at about 120 s are considered to correspond to a basic change in the growth process. These and other data suggest that at times less than 120 s the film is fully protective presumably growing by a high field mechanism. At about 120 s, breakdown of this film begins, leading to the formation and subsequent growth of a thick precipitated layer. The latter is relatively unprotective, as indicated by the deposition of copper on the platinum counter electrode, resulting from active copper dissolution during film growth. Optical microscopy of samples after the tests revealed thick black films, usually poorly adherent, some parts even flaking off during rinsing in distilled water for the samples tested at the more anodic potentials. Extensive pitting was present underneath the oxide, and multiple pits also existed in the film, Fig. 6a. At 0 and +0.1 V, variations of Δ and Ψ were similar to those observed in Fig. 5a, and generally occurred more rapidly the higher the potential. It is believed that, in this solution, the oxide relevant to T-SCC is most likely the thin protective film forming in the initial phase.

Oxide thickness was calculated from the ellipsometric data using the procedure of Green et al. [33]. Data for the acetate solution, pH 5.5, are plotted in Fig. 7*a* for potentials of 0, +0.05, and +0.1 V. Because of surface roughening and other changes, this method cannot be used after breakdown has occurred and thus each curve terminates at this time. It can be seen that the growth rate is essentially the same for +0.05 and +0.1 V, and somewhat smaller at 0 V. At the higher potential values, oxide growth is considered to be linear because



Time (s)

FIG. 4—Variation of Δ for copper {110} monocrystals exposed to 0.1 M sodium acetate at an applied potential of 0 V SCE.

film breakdown occurred before growth became limited by transport across the film. Incidentally, it is interesting to note that increasing the potential decreases the time for the onset of oxide breakdown.

1 M Sodium Nitrite—Ellipsometric studies were also conducted in 1 M NaNO₂, pH 9. The variation of Δ and Ψ with time at +0.05 V is shown in Fig. 5b. Comparison with Fig. 5a indicates that the behavior is different from that in the acetate in that there is no evidence for film breakdown. Similar observation was made at -0.15 and 0 V.

Samples observed by optical microscopy revealed thin oxides displaying interference colors. Red and blue at -0.15 V, the oxide was silvery dark blue/black at the other potentials. Films in this solution appeared to be smooth and adherent, Fig. 6b. These observations support the view that breakdown does not occur and are consistent with the low currents observed in Figs. 2 and 3, and during ellipsometric tests.

Calculations of oxide thickness were carried out, and they are plotted in Fig. 7b. It can be seen that at the lowest potential, -0.15 V, a very thin film forms immediately, but that further growth does not occur until about 300 s, when it thickens to a limiting value close to 250 Å. Growth was instantaneous at 0 and +0.05 V and the oxides rapidly attained limiting thicknesses of 280 and 400 Å, respectively. It is interesting to note that the limiting thickness of the oxide is not proportional to the applied potential.

Slow Strain Rate Tests

0.1 M Sodium Acetate—This work demonstrated that copper is susceptible to T-SCC in aqueous acetate under anodic polarization. The data for tests at pH 3, pH 5.5, and pH 10



FIG. 5—Variation of Δ and Ψ for copper {110} monocrystals exposed to (a) 0.1 M sodium acetate, pH 5.5, and (b) 1 M sodium nitrite, pH 9, at an applied potential of +0.05 V SCE.

are presented in Table 1. It can be seen that copper is immune at pH 3 while T-SCC occurs generally at pH 5.5 and 10.3, although in a few cases the overall failure was ductile at pH 5.5. Based on the data at pH 5.5, it appears that the susceptibility to T-SCC, as indicated by maximum engineering stress, elongation to failure, and nominal crack velocity, increases with increasing anodic polarization and decreasing strain rate.

Optical and SEM observation revealed that at pH 5.5 most cracks were parallel to slip traces on the free surface, Fig. 8, suggesting that initiation occurred at emerging slip steps. The primary fracture surface, on the other hand, was macroscopically perpendicular to the tensile axis. Based on previous work [6], it is likely that propagation takes place on $\{110\}$ planes. Examination of the fracture surfaces was rendered difficult by the presence of a thick oxide (presumably Cu₂O or Cu₂O/CuO as suggested by the voltammograms, Figs. 1 and 3), but it was possible in some instances to find regions that displayed cleavage-like facets, Fig. 9. At the lowest anodic potential, 0 V, numerous shallow cracks were present along slip lines at the surface but closer examination revealed that these did not propagate



FIG. 6—Optical micrographs of $\{110\}$ copper monocrystal surfaces tested in (a) 0.1 M sodium acetate, pH 5.5, at an applied potential of ± 0.1 V SCE and (b) in 1 M sodium nitrite, pH 9, at an applied potential of ± 0.05 V SCE.


FIG. 7—Time variation of the thicknesses of the oxides grown on $\{110\}$ copper surfaces in (a) 0.1 M sodium acetate, pH 5.5, and (b) 1 M sodium nitrite, pH 9.

beyond the thick oxide. At this potential, only two transgranular cracks were observed, both at the edge of the specimen where plane stress conditions prevail, and the overall mode of failure was ductile. Similar behavior was observed at higher potential, +0.05 V, and higher strain rate, $5 \cdot 10^{-6}$ s⁻¹; at even higher strain rate, $8 \cdot 10^{-6}$ s⁻¹, at this potential, no initiation was observed and failure was completely ductile.

At pH 3, crystallographic etching occurred on the specimen gage length at cathodic, -0.06 and -0.03 V, and low anodic, +0.01 V, potentials as shown in Fig. 10. Under higher anodic polarization, +0.05 V, active dissolution occurred more extensively and the solution turned



FIG. 8—Scanning electron micrographs of the free surface of a randomly oriented copper monocrystal tested in 0.1 M sodium acetate, pH 5.5, at an applied potential of +0.04 V SCE and a strain rate of 10^{-6} s⁻¹, (a) adjacent to the primary fracture (high strain), (b) further from the primary fracture. The tensile axis is vertical.



FIG. 9—Scanning electron micrograph of the fracture surface of a randomly oriented copper monocrystal tested in 0.1 M sodium acetate, pH 5.5, at an applied potential of +0.04 V SCE and a strain rate of 10^{-6} s⁻¹.



FIG. 10—Scanning electron micrograph of the free surface of a randomly oriented copper monocrystal tested in 0.1 M sodium acetate, pH 3, at an applied potential of +0.01 V SCE and a strain rate of 10^{-6} s^{-1} .

blue. No crack initiation was found in any cases and failure occurred by ductile overload. For all tests at pH 5.5, the pH change during the experiment did not exceed 0.1 except for a ten-day test at 10^{-7} s⁻¹ where the pH rose to 6.2. In this test, the solution became slightly blue, indicating the presence of cupric ions. The pH after the tests at pH 3 was always less than 3.2.

1 M Sodium Nitrite—Tests in 1 M NaNO₂ were performed at the corrosion potential and several applied potentials. Copper was found to be generally susceptible to T-SCC except when polarized cathodically at -0.15 V. Measurements of the nominal crack velocity at several potentials, Table 2, indicate that the susceptibility to T-SCC increases with increasing applied potential. This behavior is consistent with data obtained by Yu and Parkins [34] on polycrystalline samples, also given in Table 2. Our values are consistently lower than those obtained by these authors, and this may be due to shorter initiation times for polycrystals due to the availability of initiation sites at grain boundaries. It is important to mention again that these values are underestimates of the actual crack velocity since the time used in the calculation includes that for initiation. Sieradzki et al. [3] measured crack velocities between 1 and $3 \cdot 10^{-8}$ m/s by marking the crack front at known time intervals for copper monocrystals tested at 0 V.

The oxide covering the fracture surfaces appeared to be thinner in this solution than in the acetate and allowed more detailed examination. The SEM observation revealed cleavage-like facets, Fig. 11, and in some instances, crack arrest markings were observed, Fig. 12, indicating the discontinuous nature of the crack propagation. The spacing between these markings was constant and approximately 2 μ m. From this spacing and the estimated crack velocity ($\sim 10^{-8}$ m/s), the arrest period between each brittle event is approximately 200 s.



FIG. 11—Scanning electron micrograph of the fracture surface of a randomly oriented copper monocrystal tested in 1 M sodium nitrite, pH 9, at the corrosion potential and a strain rate of 10^{-6} s⁻¹.



FIG. 12—Scanning electron micrographs showing crack arrest markings observed on the fracture surface of an oriented copper monocrystal tested in 1 M sodium nitrite, pH 9, at an applied potential of +0.05 V and a strain rate of 10^{-6} s⁻¹. The direction of crack propagation is from lower left to upper right; (b) shows a magnified area of (a).

Overall optical and SEM observation of the sample gage lengths revealed a higher number of cracks in 0.1 M NaAc compared to 1 M NaNO₂, but the rate of cracking was significantly faster in the latter, Tables 1 and 2.

The solution pH, adjusted to 9 before the tests, was measured to be between 7.5 and 7.7 after the tests.

Concerning the oxide(s) in this solution, the voltammetry, Fig. 2, predicts that both Cu₂O and CuO may be present particularly at the highest potentials. However, the rather constant value of refractive index obtained from ellipsometry suggests the presence of a single oxide. It is most likely Cu₂O as proposed by previous workers [5]. At +0.05 V, however, the presence of a duplex Cu₂O/CuO or Cu₂O/Cu(OH)₂ cannot be discounted.

Discussion

Ellipsometric and voltammetric measurements carried out in 0.1 M NaAc have established that an oxide is present at pH 5.5 and 10.3, but that no oxide forms at pH 3. From these results and the slow strain rate data, Table 1, it is evident that an oxide is present when T-SCC occurs but that copper is immune in the absence of a film.

The data obtained at pH 5.5 and a potential of +0.05 V show that T-SCC can be suppressed by increasing strain rate, failure becoming completely ductile at a strain rate of $8 \cdot 10^{-6}$ s⁻¹, despite the presence of an oxide, Table 1. This behavior is attributed to a competition between T-SCC and ductile rupture. At the same pH, decreasing the potential at a constant strain rate of 10^{-6} s⁻¹ can be seen to decrease susceptibility to T-SCC as indicated by a higher maximum engineering stress and elongation to failure as well as a slower nominal crack velocity. At the lowest potential, 0 V, the overall failure becomes ductile despite the presence of an oxide, the few stress corrosion cracks formed being too shallow to play a significant role. Again, a competition between T-SCC and ductile rupture is considered to exist; decreasing the potential progressively decreases the susceptibility to T-SCC until ductile failure predominates.

In 1 M NaNO₂, pH 9, ellipsometry and voltammetry in conjunction with the slow strain rate results of Table 2 show that T-SCC is, in each case, associated with the presence of an oxide. The data of Table 2 also indicate that, as in 0.1 M NaAc, pH 5.5, increasing the potential results in increasing the susceptibility to T-SCC. Again, at the lowest potential, -0.15 V, copper is immune to T-SCC despite the presence of an oxide.

The results for the nitrite solution provide an explanation for the observed dependence of susceptibility to T-SCC on potential. The film-induced cleavage model postulates that crack propagation is discontinuous, and that a critical film thickness is required to initiate each new cleavage event [7]. Since cleavage propagates at a velocity near that of sound, the rate limiting step during crack propagation would be the growth of the oxide between brittle events. Ellipsometric measurements show that in $1 M \text{ NaNO}_2$, pH 9, the rate of growth of the oxide increases with increasing potential, Fig. 7b, thus accounting for the observed increase in susceptibility to cracking.

In 0.1 *M* NaAc, pH 5.5, the correlation between susceptibility and oxide growth kinetics is observed, except at higher potentials where the growth rate of the oxide, as measured by ellipsometry, becomes independent of potential, Fig. 7*a*, despite the fact that the susceptibility increases, Table 1. A further anomaly is observed when attempting to correlate the rate of growth of the oxide and the T-SCC susceptibility of copper in 0.1 *M* NaAc, pH 5.5, and 1 *M* NaNO₂, pH 9. The data show that the nominal crack velocity is an order of magnitude higher in the nitrite, Tables 1 and 2, even though comparable oxide growth rates are observed in these solutions, Fig. 7*a* and *b*. This behavior indicates clearly that other characteristics of the film are also important.

Voltammetric, Fig. 3, and ellipsometric studies, Fig. 5a and b, in the two solutions indicated that the oxide in the nitrite is protective, while breakdown occurs in the acetate leading to the formation of a thick, poorly protective film. The slower cracking in aqueous acetate may be attributed to the less protective oxide, although the relationship between T-SCC susceptibility and oxide protectiveness is unclear at the present time. It is possible that the thick corrosion products in the acetate limit transport within the crack, thus affecting the rate of cracking. Other characteristics of the oxide that remain to be established include the nature of the oxide (Cu₂O, CuO), its epitaxial relationship, and mechanical properties.

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DISCUSSION

*R. N. Iyer*¹ (*written discussion*)—Your results of stress corrosion cracking in copper emphasize the necessity of protective films for localized corrosion, which is a well-known phenomenon in many steels, especially stainless steels. Could you comment whether the hardness of the base material is only a secondary note to the film formation and dissolution events?

T. B. Cassagne, J. Kruger, and E. N. Pugh (authors' closure)—The question appears to be based on the view that cracking occurs by the film-rupture (or slip dissolution) mechanism, by which the crack advances by anodic dissolution following the localized rupture of a protective film. Our approach for transgranular stress corrosion cracking of copper is based on an entirely different model, namely, film-induced cleavage, whereby the presence of the film leads to the initiation of a cleavage crack for significant distances into the underlying metal. We have not investigated the effect of hardness, but it could clearly influence the initiation and propagation of the cleavage crack.

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Coherency Stress and Transgranular Stress Corrosion Cracking of Cu-18Au Alloy

REFERENCE: Fritz, J. D., Parks, B. W., and Pickering, H. W., "Coherency Stress and Transgranular Stress Corrosion Cracking of Cu-18Au Alloy," *Environmentally Assisted Cracking: Science and Engineering, ASTM STP 1049,* W. B. Lisagor, T. W. Crooker, and B. N. Leis, Eds., American Society for Testing and Materials, Philadelphia, 1990, pp. 76–85.

ABSTRACT: It has been proposed that the lattice mismatch between a dealloyed layer and the substrate alloy may play a role in the transgranular stress corrosion cracking (TSCC) of copper alloys. This investigation uses the single-exposure X-ray technique to measure the residual stress in a dealloyed layer formed by the selective dissolution of copper (Cu) from a copper-gold (Cu-18Au) alloy. The gold-rich dealloyed layer was found to have an average compressive stress of 39.3 MPa, indicative of a lattice mismatch at the alloy/dealloyed layer interface. Polycrystalline specimens of Cu-18Au that were dealloyed and then stressed during anodic polarization to relatively large overpotentials for copper dissolution showed cracking that propagated well into the substrate alloy. The cracking was predominantly transgranular, and the fracture surfaces showed features consistent with a transgranular cleavage mechanism. On the other hand, specimens that were dealloyed and then stressed while polarized to relatively low overpotentials for copper dissolution, formed cracks in the dealloyed layer that were always arrested at the alloy/dealloyed layer interface. Lateral resolution was a fraction of a micrometre (μm) , so that it was obvious that within this resolution limit there was no propagation into the bulk alloy. These results suggest that the lattice mismatch by itself is not sufficient to propagate a crack into the substrate alloy. However, results for a wider range of conditions and with improved resolution are now needed to more completely address this issue.

KEY WORDS: film-induced cleavage, stress corrosion cracking, dealloying, selective dissolution, interface strains, lattice parameter mismatch. coherency stress, copper-gold alloys, fatigue (materials), cracking, environmental effects

The copper-gold (Cu-Au) alloy system has certain characteristics that make it a model system for the study of transgranular stress corrosion cracking (TSCC). One of these is that environmental cracking mechanisms involving hydrogen can be excluded since there are well-documented analyses showing that hydrogen ion discharge is not possible for Cu-Au alloys either on the sample surface or inside a cavity open to the environment [1,2]. This is important since most studies of TSCC have been done on alloy systems in which hydrogen has to be considered as a potential embrittling agent, including studies on stainless steels, brasses, Cu-Al alloys, and all other alloys that contain base metals, although there have been claims that hydrogen can be ignored in some of these alloys.

On the other hand, there has been an accumulation of data over the years on various copper-base alloys that supports the idea of a distinct cleavage step in a discontinuous crack propagation process [3-6], including arrest markings on the fracture surface. The spacing

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of the arrest markings suggests propagation events of micrometre (μ m) dimension, and scanning electrode microscopy (SEM) fractography examination suggests cleavage-like character (river patterns and ledges). The cause of a cleavage event in normally ductile alloys is not clear. Interesting proposals that have been discussed by many researchers over the years include the ideas of vacancy formation during dealloying and their ingress into the alloy to cause local embrittlement [7,8], and local embrittlement caused by a film on the surface [3,5,6]. In models based on the latter idea, cracks form in a reaction product layer (for example, oxide or dealloyed layer) and then propagate into the substrate alloy in a cleavage-like manner until blunted upon entering an alloy region that has normal ductility. Embrittlement of the normally ductile alloy is required for the cleavage step to occur.

In the so-called film-induced cleavage model [3], embrittlement has been attributed to the inhibition of slip by, among other means, the coherency stress generated by the mismatch in lattice parameter at the interface. Once the crack is arrested, the film-induced cleavage model calls for the formation of an additional condensed reaction product at the crack tip so that another propagation event is nucleated in the layer and the cycle repeats itself. A dealloyed layer that is either brittle or ductile has been analyzed to give a cleavage-like propagation into the substrate alloy. In earlier transmission electron microscopy (TEM) observations of crack propagation in dealloyed porous thin films, the overall brittle crack propagation process appeared to occur as a ductile tearing process through the thin (10 nm) alloy walls of the porous structure [9].

There are also models of TSCC that do not require the pure mechanical cleavage that is characteristic of the film models. These are referred to as the dissolution models [9-11]. One of the earliest models of this type involves selective dissolution accompanied by porous layer formation and crack propagation through the porous dealloyed layer [9,12]. This process, in principal, could be either discontinuous, although the idea has not been developed to the point of predicting the spacing, or continuous corresponding to spacings near atomic dimensions. With the advent of TEM, Pickering and Swann [9] produced evidence of cracking within the porous dealloyed layer of thin Cu-25Au films. Later, porous, dealloyed material was identified along and ahead of stress corrosion cracks in Cu-25Au and Cu-40Au [13] and Fe-10Pt bulk samples [14]. Although the grain boundaries were not revealed, the cracks were, at least in part, transgranular based on their observed branched nature. For the Cu-Au samples [13], cracking occurred under low load conditions and, therefore, at a relatively slow propagation rate. At normal propagation rates, less copper dissolution would be expected per unit length of crack. The limit, corresponding to the highest possible propagation rate, would be copper dissolution on a monolayer scale, although some authors have argued that dissolution on a monolayer scale does not occur. They base their argument on the observation that the quasi-stationary rate of formation of the dealloyed layer is lower than the average crack growth rate [15]. Since the cracking process is discontinuous, it is, however, the current transient during the individual cracking event that is important. For example, an individual cracking event has been reported to take less than 100 μ s [3]. Under these conditions, the important current value is the transient value during the 100 μ s cracking event, not the average or quasi-stationary value.

Monolayer copper dissolution could be sufficient for atomically sharp crack propagation and cleavage-like appearances, but insufficient for producing a porous (dealloyed) layer, since the latter would require copper dissolution from a much greater thickness of material corresponding to the 10-nm scale of the porosity observed in normal dealloying processes. If or when dissolution-type mechanisms are operative, this could be the explanation for the absence of porous material on the fracture surfaces in the reported fractographic studies of TSCC in copper base alloys.

A role of current resistance (IR) drop in the crack could also be important in TSCC on

two counts, and has been considered in one of the dissolution models [14,16]. If the IR drop that is due to current flow within the electrolyte from the base of the pores to the bulk solution is reltively large as some results for analogous conditions might indicate [1,17], the local electrode potential at the base of the pores (alloy/electrolyte interface where copper is mainly dissolved from a Cu-Au alloy [8,18,19]) is less noble than at the outer surface. Thus, selective dissolution of the less noble metal, rather than simultaneous dissolution of both components is more likely at the base of the pore than at the outer surface. This IR effect has, in fact, been suggested to be the explanation of the occurrence of selective zinc dissolution at the apex of cracks but not at the outer surface during stress corrosion cracking of α -brass [16].

The second way in which the IR drop within the pores is relevant to the role of dealloying in TSCC is a consequence of the lower overpotential for the less noble metal, for example, copper in the Cu-Au system, that exists at the bulk alloy/pore interface by virtue of its less oxidizing electrode potential. If this overpotential becomes quite small, then the surface diffusion mechanism for dealloying cannot be so easily ruled out when it comes to explaining how the dealloyed layer can contain a significant concentration of the less noble metal, as has been observed for certain dealloying conditions [8, 18, 19]. The argument is that when the overpotential is very small, adatoms of the less noble metal can reside on the pore surfaces for relatively long times and accumulate by surface diffusion with noble metal atoms to form the observed alloy compositions of the dealloyed layer. This is in contrast to the usual argument [8, 18, 19] that there would be a negligible lifetime for copper adatoms since the copper adatoms would be immediately ionized in the presence of the very large overpotentials, that is, the copper adatoms would be ionized before they could diffuse along the surface to the growing nuclei of gold. Hence, the dealloyed layer would be gold rather than Cu-Au alloy.

Based on the good success of the film-induced cleavage model to explain observations during TSCC in the various systems, our goals in this work were to experimentally determine if (a) the lattice mismatch between the dealloyed layer and substrate Cu-Au alloy would produce a measurable coherency stress, and (b) cleavage-type crack propagation would occur over μ m distances into the substrate Cu-Au alloy in the absence of copper dissolution, in accord with the film-induced cleavage model.

Experimental

For these experiments, samples were cut from Cu-18Au polycrystalline alloy and annealed at 700°C for 2 h and furnace cooled. In this condition, the samples exhibited barely detectable Cu₃Au superlattice reflections in X-ray diffraction patterns. The electrolyte used for dealloying the samples was $1N \text{ Na}_2\text{SO}_4 - 0.01N \text{ H}_2\text{SO}_4$. The electrochemical behavior of this alloy/solution system is well documented [8,10,12,20]. The region of potential dependent active copper dissolution (classical dealloying) is $E > E_c \approx 750 \text{ mV}$ (SHE) at 25°C, where E_c is the breakaway or critical potential [10,20].

In order to measure the coherency stress produced during the dealloying, the singleexposure X-ray stress measurement technique [21] was used. The stress in the surface plane is given by

$$\sigma = \left(\frac{E}{1-\nu}\right) \frac{S_2 - S_1}{4R \sin^2 \theta \sin^2 \beta}$$
(1)

where E is Young's modulus, θ is the Bragg angle, v is Poissons ratio, R and β are defined in Fig. 1, and S₂ and S₁ are 2 θ displacements from the stress-free 2 θ positions for a particular set of *hkl* planes.

In order to investigate the possibility that a TSCC can propagate from a dealloyed layer



FIG. 1—Single-exposure technique uses two detectors to examine reflections from two sets of planes with the same Miller indices but at different orientations with respect to the sample surface.

into the substrate alloy in the absence of copper dissolution, experiments were done using the set up shown in Fig. 2. This is a typical three-electrode cell for setting the electrode potential on the sample in the presence or absence of a load (three-point bending) on the sample. Using this loading device, stress corrosion cracking readily occurs and was predominantly transgranular. Some segments of the cracks in Figs. 3 and 4 are seen to be transgranular and the fractographs in Fig. 5 also show the transgranular nature.



FIG. 2—Schematic of the experimental setup used in the three-point bend tests.



FIG. 3—Cross section micrograph of an etched (5% KCN-5% $(NH_4)_2S_2O_8$) Cu-18Au sample. Alloys identify some of the transgranular regions of cracking in the substrate alloy.

Results and Discussion

Table 1 lists the results of the single-exposure X-ray stress measurements on two specimens, one in the as-annealed and furnace-cooled condition and the other in the dealloyed condition. The dealloyed layer was produced by anodic polarization at $E \approx 992 \text{mV}$ (SHE) until 92 coul cm⁻² of charge were passed. A residual tensile stress of 33 to 41 MPa (5 to 6 ksi) existed in the surface following the heat treatment, and was attributed to the way in which the samples were suspended in the evacuated capsule. All measurements showed that dealloying caused a change in stress in the direction of a more compressive stress in the dealloyed layer and, indeed, resulted in 40 MPa compressive stress or a total change in stress of approximately 75 MPa. From considerations of the lattice parameter difference between copper and gold, a compressive coherency stress is expected in the dealloyed layer.

Table 2 summarizes the results of the three-point bend experiments designed to test for crack propagation from the dealloyed layer into the alloy substrate. In these experiments, a certain amount of charge was passed to form a dealloyed layer prior to the application of the bending load, either approximately 100 or 50 coul cm⁻². A constant bending load in the plastic region was then applied simultaneously with a large anodic overpotential for copper dissolution, for example, 942 mV SHE, or a low anodic (or cathodic) overpotential that was much less favorable for copper dissolution, for example, 142 mV (SHE). The results were very different for the two overpotential conditions. At the large overpotentials, cracks originating in the dealloyed layer easily propagated into the substrate alloy as shown in Fig. 4. At the low or negative overpotentials, the cracks again easily nucleated within the dealloyed layer but they showed no tendency to propagate into the substrate alloy, as illustrated in Fig. 6. For the resolution available in the microscope, on the order of a fraction of a



FIG. 4—SEM micrographs (secondary electron detector) of the cross section in Fig. 3 showing mixed intergranular and transgranular crack propagation through the dealloyed layer (D) and into the alloy substrate (A). The sample was dealloyed at E = 942 (SHE) for 102 coul cm⁻² of charge, and then stressed for 10 min while maintaining E = 942 mV.



FIG. 5—Typical SEM micrographs of the fracture surface of cracks in the substrate alloy, showing "river" patterns and parallel ledge morphology typical of a transgranular cleavage fracture.

micrometre, no cracks were observed to propagate across the dealloyed layer/alloy interface into the bulk alloy phase.

The X-ray stress measurements demonstrate the existence of a compressive stress in the dealloyed layer but its role, if any, in the TSCC process was not indicated in the three-point bend experiments. It has been shown that a coherent dealloyed layer that produces compression in the substrate alloy could theoretically cause embrittlement of the substrate alloy [3].

Measurement	ksi	(MPa)	Average ksi	(MPa)
		As-Heat-Treated	SAMPLE	
1	4.8	(33.1)		
2	5.0	(34.5)	5.2 ± 2	(35.8 ± 13.8)
3	5.9	(40.7)		
		DEALLOYED LA	AYER ^a	
1	-6.5	(-44.8)		
2	-5.7	(–39.3)	-5.7 ± 2	(-39.3 ± 13.8)
3	-4.8	(-33.1)		· · · · · · · · · · · · · · · · · · ·

TABLE 1—Residual stress measurements.

^a Sample dealloyed at E = 992 mV (SHE) until 92 coul cm⁻² of charge were passed.

Clearly, this is not the situation with the Cu-Au system where the lattice mismatch is such that compression is created in the dealloyed layers rather than in the substrate alloy. This may not, in itself, rule out the operation of the film-induced cleavage mechanism in the Cu-Au alloy system, but it does negate one theoretical argument in its favor.

What the three-point bend experiments show is that although TSCC into the substrate alloy does readily occur when copper is simultaneously dissolving within the resolution of the microscope, cracks do not propagate into the alloy in the absence of a large overpotential for copper dissolution. These results are consistent with the idea that simultaneous copper dissolution is required for cleavage-like crack propagation to occur into the substrate alloy, as proposed in the dissolution models. This is in contrast to the idea that the coherency stresses are sufficient in themselves to cause embrittlement and crack propagation into the substrate alloy. Thus, the latter point addresses the basic issue of the existing controversy regarding the mechanism of TSCC, and as such it would be desirable to have additional data of the same type (but with improved resolution) for a wider set of conditions.

Examination of the fracture surface of the cracks that propagated into the substrate alloy, showed that the cracking was very much cleavage-like and transgranular in character. River patterns and ledges were regularly seen, as illustrated in Fig. 5. Arrest markings that are so clearly visible in other reported cases of TSCC in the literature, however, were not apparent in these fractographs. Less evident arrest markings may, however, be present, for example, in the lower right of the micrograph in Fig. 5b.

Amount of Charge (coul cm ⁻²)	E versus SHE in mV and (time in min) during Three-Point Bending	Crack Penetration	
102.0	942 (10)	cracks penetrate well into the substrate alloy	
106.8	142 (10)	all cracks stopped at the dealloyed layer/alloy interface	
50.0	842 (5)	cracks penetrate well into the substrate alloy	
50.0	292 (5)	all cracks stopped at the dealloyed layer/alloy interface	

TABLE 2—Results of the three-point bend experiments.



FIG. 6—Same as Fig. 4, except the sample shows no crack propagation beyond the dealloyed layer/ alloy interface when stressed for 10 min while maintaining E = 142 mV (SHE) instead of 942 mV; b is an enlargement of a.

Conclusions

The following conclusions are reached, based on the results reported here for TSCC of Cu-18Au in $1N \operatorname{Na_2SO_4} - 0.01N \operatorname{H_2SO_4}$ solution.

1. Dealloying produced a measurable amount of compressive stress in the dealloyed layer, the source of which is considered to be the coherency stress caused by the lattice mismatch at the bulk alloy/dealloyed layer interface.

- 2. At high overpotentials for copper dissolution, cracks penetrated well into the substrate alloy, whereas in their absence, cracks stopped at the dealloyed layer/alloy interface under otherwise identical loading conditions.
- 3. In view of the preceding conclusion, these results indicate that simultaneous copper dissolution strongly promotes and, indeed, may be necessary for cleavage-like transgranular crack propagation in the normally ductile Cu-Au alloys.
- 4. Fracture morphologies show features characteristic of transgranular cleavage fracture. Arrest markings were not very evident in the fractographs.

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Role of Selective Dissolution in Transgranular Stress-Corrosion Cracking: Studies of Transient and Steady-State Dealloying in Copper-Gold Alloys

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ABSTRACT: Transgranular stress-corrosion cracking (T-SCC) was studied for disordered single crystals of Cu-25Au in 0.6 *M* sodium chloride in the potential range 0 to 600 mV (sce), over which exclusive selective dissolution of copper occurs and hydrogen generation is thermodynamically excluded. Under these conditions the strain-free anodic dissolution displays "passive" behavior below a critical ("transpassive") potential, E_c . Massive dealloying occurs above this potential, leading to the formation of a gold sponge surface layer. On the other hand, scratching experiments established that transient dealloying occurs well below the critical potential, $E_c = 430$ mV, and straining electrode tests show that T-SCC also occurs in this same passive potential domain. In the passive domain, transient surface scratching in the same corrosive environment. It is also shown that dynamic straining enhances steady-state dissolution below E_c , thus indicating that crack-related deformation could lead to enhanced dissolution in the newly-formed crack. This has implications that affect our understanding of the renucleation process in TSCC.

KEY WORDS: cracking, environmental effects, transgranular stress-corrosion cracking, selective dissolution, transient dealloying, copper-gold alloys, single crystals

It is considered that for many metal systems (notably face centered cubic (fcc)), transgranular stress-corrosion cracking (T-SCC) occurs by discontinuous cleavage. For such systems, the fracture surfaces do not lie along slip planes, as would be expected if the dominant mechanism were shear. Observation of the fracture surfaces reveals that opposing faces are nearly matching and that the surfaces are cleavage-like, displaying a distinctive "facet-step" morphology and "river markings" [1]. Further evidence includes the observation of crackarrest markings in conjunction with results obtained using pulse-loading techniques [2], and correlation of discrete acoustic-emission pulses with electrochemical noise [3]. Typical fracture surfaces for copper-gold alloys are shown in Figs. 1a, b, and c. Since a corrosive environment is a prerequisite for such fracture, a corrosion process must be involved. This

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was discussed by Forty [4], who suggested that in brass, dezincification at the tip of an arrested crack leads to local embrittlement, which in turn leads to continued crack advance. Sieradzki and Newman [5], using a two-dimensional discrete-lattice model, showed that surface modification, be it dealloying or coherent film formation, could lead to such embrittlement under the influence of the stress field of a crack tip. In their model, the misfit stress arising from dealloying, for example, leads to the formation of a crack at the interface between the underlying matrix and the surface-affected zone when the disparity between the atom sizes is sufficiently large.

Recent findings suggest that the initial nucleation step for T-SCC differs from the continued re-nucleation process associated with propagation of the crack. This initial step presumably develops the appropriate stress state and environmental conditions for T-SCC and involves the formation of a groove or crack, not necessarily of the same orientation as the ensuing transgranular crack [6]. For the case of brass in amoniacal solutions, we have seen local dissolution of active slip planes providing the necessary nucleus for T-SCC [7]. In some cases, intergranular cracks may serve as suitable nuclei for transgranular cracks. We have previously reported [8] an alternative mechanism that occurs in copper-gold alloys where a brittle gold sponge forms on the surface in both sodium chloride (NaCl) and ferric chloride solutions. Under tensile loading, cracks form in this sponge and propagate into the underlying matrix, providing the nucleus for T-SCC. Numerous other mechanisms could be suggested.

With regard to continued renucleation, which is the propagation mode of T-SCC, some mechanism is required to explain both the observed crack morphology (that is, the crack orientation, the crack-arrest markings, the details of the "river markings," etc.), as well as the observed kinetics (that is, the dependence on potential and crack-tip environment on the time between microcracking events, the crack-advance distance, etc.). Processes similar to those that lead to initial nucleation may be involved, such as selective dissolution leading to the formation of a sponge [8,9], a tarnish film [5], or a depleted surface region at the crack tip. A distinctly different process involves dissolution along slip planes intersecting the crack tip, which was suggested by Forty [4], but the detailed mechanism was unspecified. All of these mechanisms must also involve the role of stress, that is, provide the necessary stress condition for crack renucleation, as was true for the case of initial nucleation. The subsequent arrest of the renucleated crack has been explained by the activation of a slip band that absorbs the crack-driving energy [4,10]. However, it could just as easily be the consequence of a decaying crack-driving-force from a fixed crack-opening-displacement caused, for example, by the release of a dislocation pileup [11].

The foregoing account indicates that the detailed mechanism for crack propagation remains unclear. Indeed, there may be more than one mechanism that could explain the process. However, chemical dissolution is certainly involved, and the study of transient currents associated with the initial nucleation and the subsequent discontinuous cracking events seems appropriate. This paper describes the results of just such preliminary studies for coppergold alloys in aqueous NaCl, undertaken in order to elucidate some of the details of T-SCC. Results are presented for both steady-state as well as transient dealloying. In addition, results of slow strain-rate tests are presented, and an attempt is made to interpret these based on the dealloying process. The copper-gold system was chosen because exclusive dissolution of copper occurs over the investigated potential range. Also, involvement of hydrogen in the cracking process is thermodynamically excluded in this potential range.

Experimental Procedures

Experiments were done on specimens cut from a Cu-25Au single crystal, grown using the Bridgeman technique. The specimens were then wet-ground using 320 to 600 grit silicon

carbon (SiC) paper, followed by fine-polishing with a suspension of 0.5 μ m alumina particles, which resulted in bright and smooth surfaces. They were then degreased with ethyl alcohol and acetone, vacuum sealed in quartz capsules, annealed at 850°C for 120 h to assure homogenization and relieve any residual stresses, and brine-quenched to obtain a disordered structure. The final dimensions of all of the samples were 35 by 3 by 1 mm, and the tensile axes all had the same orientation, 15° off the (110) direction.

Corrosion tests were done in 0.6 *M* NaCl deaerated with hydrogen or helium using a PAR Model 173/276 potentiostat with platinum counter electrodes. Electrode potentials were measured with respect to a saturated potassium chloride (KCl) calomel electrode (sce) whose potential is +242 mV on the standard hydrogen scale. Polarization curves were obtained by measuring the current only after it reached a quasi steady state (waiting for 5 min following each 50 mV step in potential).

In some cases, the polarization curves were made on tension specimens while they were being deformed at constant strain rate, or while they were plastically relaxing after being loaded to various stress levels and above the yield point. These tests were performed in a corrosion cell that was mounted on an ATS slow strain-rate universal testing machine, which is a relatively "hard" machine in that sudden extensions of the sample would show up as a load drop.

Two types of scratching experiments were performed. In the first instance, the specimens were scratched in air, immediately submerged into the solution, while polarized at 350 mV (sce), and maintained at this potential for three days without an applied stress. The other experiment involved scratching crystals while they were submerged in the corrosive environment and anodically polarized to potentials between 100 and 430 mV (sce). The transient current pulses following scratching were measured using a Nicolet digital storage oscillo-scope.

In addition to these tests, the potential domain for T-SCC was established under slow strain-rate loading for samples polarized between 100 and 430 mV (sce). During these tests, current transients were observed and recorded with the Nicolet oscilloscope.

Microprobe observations were done using an Hitachi X-650 scanning electron microscope (SEM) having an ultimate resolution of 60 A and equipped to do electron microprobe X-ray analysis using either energy or wavelength dispersion.

Results and Discussion

Steady-State Polarization Studies

Figure 2 includes the results for polarization of an unstressed crystal of Cu-25Au in oxygenfree 0.6 *M* NaCl. The rest potential is seen to be -220 mV (sce). On anodic polarization, a low-current plateau is observed up to a critical potential, $E_c = +430 \text{ mV}$ (sce), above which a steep rise in current is noted. Similar behavior has previously been reported for this system [12] as well as for acid-sulfate solutions [13]. The phenomenon may be described as a "transpassive" transition (analogous to that occurring in systems with oxide films), in which the dealloyed (gold-rich) surface layers are no longer protective, leading to formation of a gold "sponge" and rapid dissolution of copper above E_c [9]. The subject has been reviewed by Pickering [14] and more recently by Kaiser [15]. The low rate of dissolution in the passive region is presumably due to saturation of surface kink and ledge sites by nonreacting gold atoms [16].

In a second test, measurements were carried out in the plateau region on a sample loaded to 140 MPa, slightly above the yield stress, and polarized to higher potentials until failure occurred, in the vicinity of E_c . The results are shown in Fig. 2, where it is seen that the



FIG. 2—Steady-state anodic polarization curves for Cu-25Au single crystals in oxygen-free 0.6 M NaCl: stress-free and for various loading conditions.

selective dissolution rate is from two to six times greater than that for the unstressed sample. In a third test, the specimen was prestrained in solution, but without anodic polarization, up to a stress level of 488 MPa, well above the yield stress. At this point, the sample was anodically polarized until failure occurred. The resulting current is also shown in Fig. 2, and it is seen to be more than an order of magnitude above the previously determined plateau. It should be noted that while this test was done under a zero imposed strain rate, in fact extensive straining was occurring, as was evidenced by a continuing load drop as the sample relaxed. Finally, two samples were polarized, one at 380 mV and the other at 400 mV, while being deformed at a constant strain rate $(1.3 \times 10^{-6}/s)$. These results are also shown in Fig. 2, where they are seen to lie along the continuation of the polarization curve for the heavily predeformed sample, that is, the sample that was observed to be deforming by creep.

There is evidence [7] that dynamic straining leads to enhanced dissolution, presumably at the surface steps exposed by dislocations emerging from the surface, or on "active" slip planes. The latter remain catalytically more active than the bulk material until the defects generated by the passage of dislocations have a chance to anneal out. But whether this can explain the preceding results is uncertain: the strain rate under the relaxing load at the higher stress level has not been measured, so it is not known if the effect is one of strain rate, per se, or simply due to the higher stresses involved.

Scratching Experiments

Several authors have suggested that dealloying occurs only above the critical potential, $E_c[14,17]$. However, Cu-25Au crystals, scratched in air and immediately anodically polarized in 0.6 *M* NaCl solution at 350 mV (sce), well below E_c , exhibited gold enrichment in the scratched region. This was confirmed by SEM microprobe analysis, which indicated extensive dealloying in the scratch, as shown in Table 1. More important, though, was the observation that cracks were formed in this dealloyed region, perpendicular to the scratch, and that these cracks even extended into the unscratched region (Fig. 3). No cracks were observed on crystals that were scratched but not immersed in the solution, nor was sponge or cracking detected in samples (or regions) that were immersed unscratched, even after 17 days exposure at 350 mV (sce). Thus, it seems that in the proper environment, residual stresses or plastic strain or both caused by scratching can lead to dealloying, and we suspect that this, in turn, leads to cracking that can initiate T-SCC.

To study the scratching behavior more carefully, the corrosion current was monitored for samples scratched while they were immersed in solution, as a function of imposed potential. A rapid rise in current accompanied the scratching, followed by a current decay at a rate related to the imposed overpotential (Fig. 4). The area exposed by scratching was not measured in each case, but the procedure was identical. This involved scratching across the entire specimen surface each time. The pressure exerted during the scratching was assumed to be the same, but variations in this pressure would lead to variations in exposed surface as well as in the related deformation and resulting residual stresses. A measure of such variation can be deduced from the measured transient peak heights, and since these varied linearly with overpotential with relatively little scatter (Fig. 5), it was assumed that the variation in scratched area was not significant. The measured projected area of the scratch was 0.12 mm².

The transient current for such a test is presented in a log-log plot as Curve a in Fig. 6. The initial and final slopes of such plots are very sensitive to the choice for the origin of the transients, which is ambiguous since the scratching takes a finite time (~ 5 ms). A proper analysis requires that the total current be deconvoluted into the current associated with each incremental area exposed as the scratch advances. For the purposes of our discussion an "average" time was chosen for the origin, corresponding to the time when the current had risen to half the peak height. This resulted in a slope of -1. The kinetic process that this describes is not clear, but it might be associated with boundary-layer charging or charge transfer under a decreasing surface concentration of copper atoms. There is an indication

	Weight, %		Atomic, %	
	Cu	Au	Cu	Au
Matrix	49	51	75	25
Scratched region	30	70	57	43

TABLE 1-Variation of copper and gold composition on the matrix and the scratched region.



FIG. 3—Scanning electron micrograph of scratched region for Cu-25Au crystal, scratched in air and immersed in 0.6 M NaCl for three days at 350 mV, well-below E_c . Note cracks in scratched region some of which propagate into the unscratched matrix.

that at very long times the slope becomes $-\frac{1}{2}$, characteristic of a diffusion-controlled process, for example, the migration of copper ions in the solution. All of this must be considered speculative. Efforts are presently being made to investigate these kinetics.

Constant Strain-Rate Tests

Transient current pulses were also observed when specimens were deformed at a constant strain rate in 0.6 M NaCl at various imposed potentials at or below E_c . These pulses were observed to coincide with load drops, which would be indicative of deformation "bursts." that occur when the renucleated crack is arrested, in light of the "hard" tension machine we were using. These pulses generally superimposed into groups, but where they could be observed as isolated pulses (Fig. 7) they appeared similar to those observed in the scratching experiments. Again, a representative transient current is displayed in a log-log plot as Curve b in Fig. 6. The kinetics of these transients were seen to be similar to those observed in the scratching experiments, with the exception that the rise times of these transients are much sharper, and there seems to be no upturn in slope at the higher times. The sharp rise-time



FIG. 4—Current transients following scratching Cu-25Au crystals immersed in oxygen-free 0.6 M NaCl and anodically polarized to various potentials below E_c (background current of ~1 microampere subtracted). The ripple in the curve is due to instrumentational artifacts.

would be expected if the process involves a cleavage event, and for small crack advances the diffusion-controlled current would be lost in the background signal. From this data, we can infer that the scratching experiments adequately model the cleavage event, and the current transients during constant strain-rate tests reflect the sudden exposure of new surface to the corrosive environment. Interpretation of the data displayed in Figs. 4 and 6 show that the magnitude of the transient current *density* during crack extension is on the order of its value during scratching, and both are enhanced as a consequence of the high slip activity associated with the process. While intense slip activity at the arrested crack tip would lead to even higher current densities in that region, the relatively small area involved would result in negligible contribution to the total observed current. It seems obvious that the occurrence of the transients is an indication of a cleavage event, and their magnitude may give a measure of the crack advance involved.

Figure 8 shows the effect of the applied potential on the time to failure, which is seen to approach zero as E_c is approached. At potentials below 300 mV the failure mode in these constant strain-rate tests is ductile and essentially unaffected by the environmental conditions. The fracture surfaces shown in Fig. 9 are illustrative of the characteristic morphological





FIG. 6—Log-log plot of transient current response for Cu-25Au in 0.6 M NaCl (a) following scratching at 300 mV (see Fig. 4); (b) following discontinuous crack advance at 400 mV during slow strain-rate testing (see Fig. 7).



FIG. 7—Transient current response following discontinuous crack advance at 400 mV in 0.6 M NaCl during a slow strain-rate test $(1.3 \times 10^{-6}/s)$. (Background current of ~100 microamperes subtracted.)

features associated with cleavage-like fracture, and they demonstrate the occurrence of T-SCC at potentials above 300 mV but well below E_c . The time-to-failure as a function of strain rate is shown in Fig. 10 for two different potentials, 300 and 380 mV. The upturn of the curve at 300 mV at the higher strain rate is indicative of reaching an upper limit of the strain-rate "window of susceptibility" at this potential, an effect which is not observed at the higher potential, closer to E_c . The data for these samples are replotted as strain-tofailure versus strain rate in Fig. 11. If the crack velocity were constant throughout a given test, one would expect a linear relationship, with a smaller slope for the more "active" environment (380 mV). In fact, the slope for the samples tested at 380 mV is essentially zero, indicating that the velocity is indeed very high. The apparent slight decrease in ductility with strain rate, if it is to be believed, may be more a reflection of the effect of strain rate on nucleation time than on the subsequent velocity. The slope for the samples tested at 300 mV indicates a slower velocity, as would be expected. The slight upturn may be an indication that at the higher strain rate the corrosion process, whatever mechanism is operative, is beginning to be overwhelmed by the higher rate of plastic deformation, resulting in an increased ductility. Thus, there is a suggestion of a potential-dependent nucleation strain, and strain rate seems to have little effect at more active potentials. This is a major focus in our research.



FIG. 8—Time-to-failure versus potential for samples anodically polarized to potentials below E_c during slow strain-rate testing $(1.3 \times 10^{-6}/s)$.

Concluding Remarks

A comparison of the transient behavior shows that the kinetics of the dissolution process during T-SCC are the same as for a surface newly exposed by scratching. It is found in other systems that dynamic straining markedly affects the dissolution process [7]. Thus, it is expected that the enhanced slip activity in the newly-formed crack surfaces would lead to high dissolution rates there, giving rise to the high current transients that are observed during cracking. The actual mechanism by which this enhanced dissolution leads to renucleation of the cleavage event is not yet known. It is expected that the "burst" of deformation associated with the arrest of the crack would result in high dissolution rates localized at the crack tip (but masked by the overall dissolution activity), setting the stage for the renucleation event. Observation of the details of current transients that coincide with cleavage events allows one to study the details of these events and their time sequence [18].



Fig. 9—SEM micrographs showing fracture surfaces of crystals deformed under slow strain rate and anodic polarization (380 mV): (a) 1.3×10^{-7} , $s_{1,2}^{-1}$ (b) 1.3×10^{-6} /s; and (c) 2.6×10^{-6} /s.



FIG. 10—Time-to-failure versus strain rate for Cu-25Au samples anodically polarized and maintained at potentials below Ec: (a) 300 mV, (b) 380 mV.



FIG. 11-Results from Fig. 10 replotted as strain-to-failure versus strain rate.

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Material Performance—I

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Effects of Electrochemical Potential on the Slow Strain Rate Fracture of 4340 Steel in a Combustion Product Residue

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ABSTRACT: Steel breech chambers in cartridge-ignition aircraft engine starters have failed in service by fracture of the chamber dome during firing. The interior surface of the dome is subject to corrosion because of accumulation of combustion products and moisture behind heat shields in the chamber. The residue collected from behind the heat shields of 25 used but still serviceable breech chambers was employed as an environment for slow strain rate tension tests of 4340 steel heat treated to the strength of the chamber. The residue contained ammonium chloride, potassium chloride, and the oxides of iron as major components. The slow strain rate tests were carried out at controlled electrochemical potentials both anodic and cathodic to the corrosion potential of -550 mV SCE (saturated calomel electrode). The tests demonstrated that the corrosion potential is at the edge of the stress-corrosion cracking potential range for the steel in this environment. Thus, stress-corrosion cracking appears to be a factor in service failures of the chambers.

KEY WORDS: corrosion, stress-corrosion cracking, steels, 4340 steel, combustion products, solid propellants, slow strain rate testing, constant extension rate testing, electrochemical potentials, fatigue (materials), cracking, environmental effects

Some military aircraft use a cartridge ignition starter system for emergency engine starts. A solid propellant cartridge is placed in a cartridge chamber/breech chamber assembly and electrically ignited. The expanding gases generated from the burning cartridge provide the necessary energy to start the jet engine. Rupture of the steel breech chamber during a cartridge burn is a matter of serious concern since it could abort the mission and cause serious damage to the aircraft. A number of such failures have been examined [1,2].

The breech chambers are constructed of steel, UNS G43400, heat treated to a hardness level of 40 to 45 HRC. Service failures have been primarily of the type shown in Fig. 1, wherein the chamber dome splits open. The fracture typically initiates in the shoulder (also called knuckle) region of the chamber, diametrically opposite the exhaust port. The fracture propagates around the circumference of the dome toward the exhaust port and the top of the dome is bent away from the chamber to form a flap.

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The chamber dome is shielded from the hot gases in the breech chamber by two Inconel heat shields welded inside the chamber. The outermost heat shield can be seen inside the chamber in Fig. 1. The heat shields limit the temperature of the inside surface of the dome to 260 to 425° C during a typical 18 to 20 s cartridge burn [3]. The pressure in the chamber will reach about 8.3 MPa. The heat shields are not pressure bearing elements in the system. There is an opening around the exhaust port to equalize the pressure behind the heat shields. Through this opening, cartridge combustion products can deposit between the heat shields and the chamber dome. Cleaning behind the heat shields and removal of these residues is virtually impossible.

Corrosion has been identified as a significant factor in most of the service failures because of the corrosion products and pitting found on the inside surface of the chamber dome. Stress-corrosion cracking was suggested as a possible failure mechanism [1,2], although erosion of the fracture surfaces by escaping hot gases makes it difficult to detect preexisting flaws or cracks or both at the fracture origin.

Residues collected from behind the heat shields of several of the breech chambers that had failed in service have been analyzed [3]. The residue consists of combustion products from the solid propellant cartridges and corrosion products from the breech chamber. This is a complex environment. In addition to the several ferrous compounds identified, the residue contained ammonium nitrate (NH₄NO₃) and potassium chloride (KCl). The residue was acidic, pH 2.8. The moistened residue was used as an environment in slow strain rate tension tests to determine the susceptibility of the breech chamber steel to environmentally assisted cracking [4,5]. A minimum in the ductility was observed at an intermediate strain rate (1.6 \times 10⁻⁶/s), indicative of a stress-corrosion cracking mechanism [6].

A recent study of 25 breech chambers removed from service and hydraulically pressurized to failure, revealed that subcritical cracks exist in the chamber dome and that they initiate from corrosion pits [7,8]. A finite element fracture analysis showed that semi-elliptical cracks in the shoulder region of the chamber dome could grow under the stresses present at the internal operating pressure of 8.3 MPa [7].

The present study was undertaken to further clarify the processes responsible for the chamber fractures. This was possible as additional quantities of residue became available from the chambers removed from service for the hydraulic testing. Slow strain rate tension tests were run in the residue to determine the sensitivity of the steel to cracking in the residue environment. To help distinguish between a hydrogen embrittlement mechanism and a stress-corrosion cracking mechanism of fracture, slow strain rate tests were also conducted at controlled electrochemical potentials.

Materials and Procedures

Analysis of Residues

The breech chambers taken from the field were considered serviceable chambers. They had been in service for undetermined lengths of time and had undergone an undetermined number of firings. The residue from each of the 25 chambers was individually analyzed by X-ray diffraction.

The X-ray diffraction patterns were quite complex. Because of the number of compounds present in the residues, some only in trace quantities, only compounds present in substantial quantities could be identified. The principal compounds identified in the residues were KCl, ammonium chloride (NH₄Cl), magnetite (Fe₃O₄), ferric oxide (Fe₂O₃), and iron oxide hydroxide (FeOOH).


Specimens of each of the residues were tested for pH. This was accomplished by moistening the residue with distilled water just enough to make a determination (0.5 mL of water per gram of residue). The pH of the residues varied from 3.5 to 8.2. The residues were then combined and homogenized to provide enough material for the slow strain rate tests. The pH of the combined residues was 4.9. The pH of the combined residue was remeasured after further dilution by factors of 2, 5, and 10. There was no shift in pH within the precision of the measurements for dilutions up to a factor of five.

Slow Strain Rate Tension Tests

Steel Specimens—Tension specimens were machined from UNS G43400 aircraft quality steel bar stock 0.64 cm diameter. The specimens were 15 cm long with threaded ends. The gage length was 1.2 cm and the gage diameter was 0.30 cm giving an L/D ratio of 4. The specimens were machined with the gage diameter slightly oversize and then heat treated to 41 to 42 HRC. The gage length was then ground to the final diameter and polished longitudinally through corundum papers E4/0 grit.

Test Cell—Because of the small quantities of the residue available, it was necessary to minimize the volume of the test cell surrounding the tension specimen. The cell used was merely a piece of glass tubing 2 cm in diameter by 5 cm long. The tube was sealed to the tension specimen at the base. This cell was filled with a test solution (more like a slurry) consisting of the breech chamber residue diluted with distilled water 2 to 1 by weight.

For tests at controlled electrochemical potentials, stainless steel foil was used to line the inside of the glass cell to serve as the auxiliary electrode. The cell was connected to a saturated calomel reference electrode through a salt bridge consisting of plastic tubing filled with agar gel. A potentiostat was used to control potentials. Tests were run at seven potentials: the corrosion (unpolarized) potential, three 100-mV increments anodic to the corrosion potential, and three 100-mV increments cathodic to the corrosion potential. The corrosion potential was -550 mV versus the saturated calomel electrode (SCE). To minimize the current required to maintain potential, the tension sample was coated so that only the gage length was exposed to the environment.

Test Machine—Tests were conducted on a W T Specialty Co. P2000 constant extension rate machine with a crosshead speed range between 10^{-6} and 10^{-9} m/s and a maximum load capability of 1000 kg. Three extension rates were employed, corresponding to nominal strain rates in the gage length of the tension specimens of 2×10^{-5} /s, 4×10^{-6} /s, and 8×10^{-7} /s.

Results

The results obtained for the slow strain rate tests in the residue are presented in Tables 1 through 3. Each table provides data for one of the three nominal strain rates. Results are also presented for tests run in oil to provide baseline data for each strain rate.

The test results reported include ultimate tensile strength, UTS, time to failure, t_F , and percent reduction in area, %RA. Because of the uniform corrosion of the gage length of the tension specimens at the anodic potentials, the reduction in area at fracture was corrected for the reduction in area away from the necked region due to corrosion. If D_0 is the initial

Electrode	Tensile	Time to	Reduction in Area, %					
mV versus SCE MPa h		$\overline{(D_1/D_0)}$	(D_2/D_0)	(D_1/D_2)				
oil	1292	4.61	56.92	1.94	56.11			
	1290	3.88	55.16	1.60	54.47			
-250	1176	4.80	59.07	10.47	54.26			
	1228	4.35	62.47	8.41	59.05			
- 350	1231	5.02	52.70	8.77	48.13			
	1242	4.37	50.52	6.51	47.12			
-450	1265	4.55	52.84	3.62	51.03			
	1262	5.23	45.80	8.36	40.82			
-550^{a}	1293	4.04	54.66	2.94	53.23			
	1285	4.08	57.19	4.12	55.26			
	1289	3.96	52.85	2.35	51.67			
-650	1299	5.38	53.78	1.27	53.21			
	1302	5.95	54.06	0.55	53.75			
-750	1273	5.26	44.90	3.90	42.65			
	1282	4.58	46.57	2.99	44.93			
- 850	1304	5.01	26.87	1.44	25.72			
	1288	4.89	40.41	0.55	40.09			

TABLE 1—Effects of electrode potential on tension tests performed at a nominal strain rate of 2×10^{-5} /s on 4340 steel in the breech chamber residue.

^a Corrosion potential.

Electrode	Tensile	Time to	Reduction in Area, %				
mV versus SCE	MPa	h h	(D_1/D_0)	(D_2/D_0)	(D_1/D_2)		
oil	1280	22.68	55.16	3.03	53.75		
	1307	21.32	57.06	1.45	56.37		
-250	1088	21.20	58.70	19.31	48.75		
	1126	19.20	48.15	13.99	39.64		
- 350	1138	17.53	29.64	9.78	22.04		
	1139	16.86	24.12	10.78	14.98		
-450	1203	17.08	30.03	3.06	27.24		
	1177	18.83	38.78	10.04	32.00		
-550^{a}	1295	21.33	56.08	1.82	55.26		
	1304	19.66	44.97	0.54	44.67		
	1292	21.38	52.56	0.72	52.22		
-650	1265	20.30	42.69	1.09	42.02		
	1304	24.75	55.83	3.78	54.10		
-750	1302	26.08	41.95	2.89	40.16		
	1311	28.33	52.98	0.55	52.71		
- 850	1309	27.30	31.13	0.72	30.63		
	1311	26.50	24.23	0.54	23.87		

TABLE 2—Effects of electrode potential on tension tests performed at a nominal strain rate of 4×10^{-6} /s on 4340 steel in the breech chamber residue.

^a Corrosion potential.

Electrode	Tensile	Time to	Reduction in Area, %				
mV versus SCE	MPa	h h	$\overline{(D_1/D_0)}$	(D_2/D_0)	(D_1/D_2)		
oil	1315	107.5	54.66	0.91	54.19		
-250	676	44.4	61.77	40.91	35.38		
-350	845	50.0	46.02	26.82	26.24		
-450	916	67.1	43.62	20.35	29.16		
- 550°	1269	109.9	45.19	4.03	42.93		
-650	1304	151.6	41.73	0.91	41.11		
-750	1309	172.0	49.35	1.45	48.75		
-850	1304	136.9	20.50	3.24	17.78		
	1307	110.0	21.84	2.36	19.98		

TABLE 3—Effects of electrode potential on tension tests performed at a nominal strain rate of 8×10^{-7} /s on 4340 steel in the breech chamber residue.

" Corrosion potential.



FIG. 2—Ultimate tensile strength versus electrochemical potential for 4340 steel in the breech chamber residue. Results compared for three strain rates.



FIG. 3—Percent reduction in area corrected for uniform corrosion versus electrochemical potential for 4340 steel in breech chamber residue. Results compared for three strain rates.

diameter, D_1 is the final diameter at the fracture, and D_2 is the final diameter away from the necked region, then $\Re RA(D_1/D_0)$ is the reduction in area at the fracture neglecting uniform corrosion, $\Re RA(D_2/D_0)$ is the reduction in area of the gage length away from the fracture due to uniform corrosion (and uniform elongation), and $\Re RA(D_1/D_2)$ is the reduction in area at the fracture corrected for uniform corrosion.

The reduction in area due to uniform elongation is about 3% or less as indicated by $\[mathcal{\%}RA(D_2/D_0)\]$ for the samples tested in oil or at cathodic potentials. The reduction in area due to corrosion increases with decreasing strain rate (longer time to failure) and more anodic potential. The reduction is about 40% at the slowest strain rate at an electrode potential of -250 mV, Table 3. This uniform reduction in area due to corrosion is reflected in the apparent tensile strength calculated from D_0 and the maximum load, Fig. 2. At potentials more anodic than -550 mV, the corrosion potential, the tensile strength decreases with increasing anodic potential shift and decreasing strain rate.

The reduction in area corrected for uniform corrosion, $\% RA(D_1/D_2)$, is plotted versus electrochemical potential in Fig. 3. There is a minimum in the reduction in area at a potential between -400 and -300 mV and the reduction is greatest at the intermediate strain rate,



FIG. 4—Percent reduction in area corrected for uniform corrosion versus strain rate for 4340 steel in breech chamber residue. Results compared for the corrosion potential (-550 mV SCE) and three potentials anodic to the corrosion potential.

 4×10^{-6} /s. There is also a sharp decrease in the reduction in area at -850 mV. This decrease is greatest at the slowest strain rate. Strain rate has very little effect in the potential range -750 to -550 mV.

The reduction in area corrected for uniform corrosion is plotted versus strain rate in Figs. 4 and 5. Figure 4 shows the data obtained without polarization at the corrosion potential, -550 mV, and at potentials more anodic than the corrosion potential. Figure 5 shows the data obtained at the corrosion potential and at potentials more cathodic than the corrosion potential. There is a minimum in reduction in area at the intermediate strain rate at a potential of -350 mV, Fig. 4. The reduction in area is small at -850 mV and decreases with decreasing strain rate, Fig. 5.

Time to failure, Tables 1 through 3, appears to correlate with corrosion rate and to a lesser extent with ductility at fracture. At the highest strain rate, the time to failure is relatively independent of the test conditions. At the intermediate strain rate, the time to failure increases with cathodic polarization and is a minimum at the anodic potentials of -350 to -450 mV. At the slowest strain rate, time-to-failure decreases markedly with



FIG. 5—Percent reduction in area corrected for uniform corrosion versus strain rate for 4340 steel in breech chamber residue. Results compared for the corrosion potential (-550 mV SCE) and three potentials cathodic to the corrosion potential.

anodic polarization and increases with cathodic polarization except at -850 mV where the ductility is quite low.

Scanning electron microscope (SEM) examination of the gage length surfaces and of the fractures revealed a picture consistent with the preceding observations. High magnification views of the surfaces of specimens strained at 8×10^{-7} /s are shown in Fig. 6(a-h). Side profiles of the fractures at low magnification are shown in Fig. 7(a-h). The specimens anodically polarized are heavily attacked with deep trenching, Fig. 6(a,b,c). The specimen at the corrosion potential, Fig. 6d, shows superficial corrosion attack, while the cathodically polarized specimens, Fig. 6(e,f,g) are free of apparent corrosion but exhibit some superficial cracking. The surface of the specimen tested in oil, Fig. 6h, is shown for comparison. The specimen tested in oil exhibited a cup and cone fracture, Fig. 7h. The specimen tested at -350 and -450 mV, Fig. 7(b,c) exhibited brittle fractures. The specimen tested at -250 mV, Fig. 7(d,e,f) exhibited at -550, -650, and -750 mV, Fig. 7(d,e,f) exhibited substantial necking before fracture. The specimen at -850 mV, Fig. 7g, had a brittle fracture.

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FIG. 6—Gage length surfaces of specimens tested at a strain rate of $8 \times 10^{-7}/s$ in the breech chamber residue. Specimens tested at various electrode potentials and in oil (SEM photographs).

Discussion

The slow strain rate test results appear to be consistent with a process of stress-corrosion cracking at the anodic potentials of -450 to -350 mV. The concept of a potential range over which stress-corrosion cracking will occur has been discussed by Uhlig [9]. He observed that for some metal-solution combinations, stress-corrosion cracking is avoided by polarizing not only below a certain critical potential or potential range, but also at potentials more



noble than the critical range. The concept is consistent with the stress-sorption theory of stress-corrosion cracking, wherein adsorption of damaging ions on mobile defect sites is optimum within a relatively narrow range of potentials. From a purely mechanical viewpoint, it is possible that at the more anodic (noble) potentials, where uniform corrosion is rapid, surface defects are unable to produce the stress risers necessary to initiate and sustain localized crack growth.

The more severe reduction in ductility at the intermediate strain rate, 4×10^{-6} /s, is also indicative of a stress-corrosion cracking mechanism. Parkins [10] has proposed that at strain

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FIG. 7—Side views of fractured tension specimens tested at a strain rate of $8 \times 10^{-7}/s$ in the breech chamber residue. Specimens tested at various electrode potentials and in oil (SEM photographs).

rates less than the optimum to support crack growth the rate of film repair must exceed the rate of film rupture.

The brittle fracture at the cathodic potential of -850 mV is consistent with a process of hydrogen embrittlement (hydrogen-induced cracking). In a solution with a pH of 4.9, hydrogen will be reduced at potentials more negative than -532 mV. Thus, there must be a substantial rate of hydrogen reduction with accompanying absorption into the steel at -850 mV. The observed increase in embrittlement (reduced reduction in area) with decreasing strain rate is a consequence of the greater hydrogen absorption with time at the slower strain



FIG. 7-Continued.

rates and the increased time for hydrogen diffusion within the metal lattice. The hydrogen diffuses to regions of stress concentration near a crack nucleus until the concentration reaches a damaging level [11]. A crack initiates when the hydrogen atoms cause slip interference or reduce the bond strength between atoms. The mobile hydrogen can then diffuse to imperfection arrays beyond the crack tip and reinitiate the process producing discontinuous crack growth. The slower the strain rate, the greater the embrittlement.

The test results indicate that the corrosion potential is just at the edge of the stresscorrosion cracking potential range for the steel in the residue environment. This result is slightly at odds with results obtained earlier [4,5], using residues from failed breech chambers, which indicated that stress-corrosion cracking could occur at the corrosion potential (also -550 mV). The major difference between the residues is the pH. It averaged less than 3 for residues collected from failed chambers and 5.8 for those removed from the serviceable chambers and used in these tests. The test results do support the view that stress-corrosion cracking rather than hydrogen embrittlement is a factor in breech chamber failures.

Conclusions

Slow strain rate tests carried out at controlled electrochemical potentials demonstrated the stress-corrosion cracking susceptibility of 4340 steel, 41 to 42 HRC, in an environment consisting of moistened residue removed from behind the heat shields in cartridge-ignition starter breech chambers. The residue contained ammonium chloride, potassium chloride, and the oxides of iron as major components. The corrosion potential of the steel is at the edge of the potential range for stress-corrosion cracking in this environment. These observations support the view that stress-corrosion cracking is a factor in the service failures of breech chambers.

Acknowledgment

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Environmental Acceleration of Fatigue Crack Growth in Reactor Pressure Vessel Materials and Environments

REFERENCE: Van Der Sluys, W. A. and Emanuelson, R. H., "Environmental Acceleration of Fatigue Crack Growth in Reactor Pressure Vessel Materials and Environments," Environmentally Assisted Cracking: Science and Engineering, ASTM STP 1049, W. B. Lisagor, T. W. Crooker, and B. N. Leis, Eds., American Society for Testing and Materials, Philadelphia, 1990, pp. 117–135.

ABSTRACT: This paper presents the results of experiments to determine which variables have the most effect on environmentally assisted cracking (EAC) of reactor pressure vessel steels. Four heats of SA508 and three heats of SA533 were studied in 288°C pressurized water reactor, light water reactor, and boiling water reactor environments. The sulfur content of these materials ranged from 0.004 to 0.025%. The most important variable was found to be the sulfur content and sulfur morphology of the material. A material with a bulk sulfur content greater than 0.010% may be susceptible to EAC. The loading frequency was found to be an important variable. Minor effects of EAC were attributed to the load ratio, ΔK level, and oxygen content of the environment. An experimental method to introduce sulfur directly to the crack tip is described. A time-based method of data interpretation is discussed.

KEY WORDS: fatigue (materials), corrosion fatigue, crack propagation, pressure vessel steels, environmental effects, environmentally assisted cracking, aqueous environments, cracking

Environmentally assisted cracking (EAC) in pressure vessel steels has been the subject of many research projects over the last 25 years [1-9]. During that period, a significant effort has been made in studying the phenomena in nuclear pressure vessel materials in simulated reactor environments. The vast majority of this work has been on EAC under fatigue loading conditions.

The work described in this paper has been performed over the last ten years under sponsorship of the Electric Power Research Institute (EPRI). The objective of this program has been to determine which variables have an influence on EAC under fatigue conditions in reactor pressure vessel steels and to quantify the effect of these variables. The information presented here has been obtained from tests on seven heats of reactor pressure vessel steels. Four of these heats are SA533 plate material and three heats are SA508 forging material. The fatigue crack growth tests have all been conducted using a computer-controlled, constant ΔK testing procedure so that the quantitative effects of changing significant variables could be measured. The tests have been conducted in both simulated boiling-water reactor (BWR) and pressurized-water reactor (PWR) environments at 288°C.

The most important variable was found to be the sulfur content of the test material. Materials with bulk sulfur content above 0.010% have a likelihood of being susceptible to

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EAC. The susceptibility of individual heats depends on both the sulfur content and the sulfide morphology. The second variable of importance is the loading frequency. For each applied ΔK level, there is a range in loading frequencies over which EAC can exist. After these two variables, there are a host of others exerting some influence on the existence of EAC. These include oxygen content and flow rate of the environment, *R* ratio of the loading wave form, and ΔK level.

The pressure vessel steels studied in this project contained a range of dissolved sulfur content from 0.004 to 0.025%. Also, a series of experiments was performed in which the sulfur was artificially introduced into either the bulk autoclave environment or the crack tip in attempts to produce EAC. These attempts were successful when the sulfur was introduced into the crack tip.

Experimental Procedures

All experiments were conducted in 76-L Type 316 stainless steel autoclaves with 51-mmthick (2T) compact fracture specimens. Each autoclave operated as a once-through refreshed system with a flow rate of simulated light-water-reactor (LWR) water of 2 L/h. Water of the desired chemistry was made up and stored in a stainless steel reservoir with a cover gas of either hydrogen or nitrogen. Specifications for both the simulated BWR water and PWR water are presented in Table 1. These specifications are service specifications in the case of a BWR. In the case of a PWR, where boric acid and lithium contents are changed throughout the fuel cycle to control the reactivity of the core, the chemistry is typical of that found at the mid-range of the cycle.

A computer-controlled servohydraulic system was used to supply the required force during the experiments. A hydraulic actuator mounted above the autoclave transmitted a cyclic tensile load to the compact fracture specimen via a load rod through a seal in the autoclave head assembly. The load on the specimen was measured by a load cell outside the autoclave. The specimen (along with a displacement transducer) was mounted in a clevis and loading pin arrangement. This displacement transducer, consisting of a tapered beam on which two high-temperature strain gages are attached, was mounted on the specimen so that it could monitor the front face deflection.

Operation of the test facility is detailed in Ref 10.

Crack lengths were determined by measuring the unloading compliance of the specimen.

	BWR	PWR
Inlet dissolved oxygen, ppm	0.35 to 0.40	
Effluent dissolved oxygen, ppm	< 0.010	
Boric acid, ppm		5700
Lithium, ppm		2.0
Dissolved oxygen, ppm		< 0.01
pH	6.5 ± 0.5	6.5 ± 0.5
Conductivity, µmhos/cm	<1	<20
Chloride, ppm	< 0.1	< 0.1
Fluoride, ppm	< 0.1	< 0.1
Dissolved hydrogen, standard		
cm ³ /kg H ₂ O		15 to 50
Reservoir cover gas	$1\% O_2$ in N_2	H_2

TABLE 1-BWR and PWR specification for the simulated BWR and PWR water chemistries."

^a Standard service chemistry specifications for BWR, and typical mid-range of fuel cycle for PWR.

The compliance of the specimen is the change in deflection per change in load and can be correlated to crack length.

All experiments were run under constant ΔK conditions, an approach that differed substantially from that used in previous fatigue crack growth investigations of pressure vessel materials. In the constant ΔK approach, a computer is used to control a fatigue crack growth experiment. The computer records the crack length and loading cycle and adjusts the load amplitude (ΔP) so that the range in stress intensity factor (ΔK) applied to the specimen is constant. The advantage of the constant- ΔK technique over the constant-load-amplitude approach is that the crack growth rate is measured under a mechanical steady state. Therefore, if ΔK is rate controlling, a constant crack growth rate should be observed in a constant- ΔK test, and step changes of test variables (such as loading frequency) can be made to study directly their effects on crack growth rates. In this way, high-quality quantitative information can be obtained on the influence of specific test variables. Constant- ΔK crack growth rate measurements techniques and computer-controlled fatigue experiments are detailed in Refs 10 through 12.

Test Materials

Fatigue crack growth experiments have been performed on seven heats of reactor pressure vessel steels. Four of the heats are SA533 GrB Cl1 (that is, Class 1) material and three heats are SA508 Cl2 (that is, Class 2) material. The chemical analysis of these materials is shown in Table 2. Most of the test material was obtained from nozzle cut-outs, and one of the SA508 heats is from a nozzle forging. The sulfur content of the SA508 material ranged from 0.012 to 0.021% (by weight), while a wider range from 0.004 to 0.025% was measured in the SA533 heats.

The room-temperature tension test properties of the test material are shown in Table 3. Complete physical property data (Charpy V impact, fracture toughness, and tensile data over a range of temperatures and specimen orientation) may be found in Ref 13. All materials were of similar grain size (predominantly ASTM 6 to 8), and possessed a bainitic microstructure with considerable amounts of blocky ferrite. Details of the microstructure of most of these materials are found in Ref 14. Quantitative metallographic analyses of the materials revealed inclusions of manganese sulfide (MnS), plus small quantities of corundum, silica, calcium oxide, and a manganese-aluminum sulfide. This study, however, addresses only the effect of the highest inclusion content, MnS, on the crack growth rate.

					, u		- · ·			
Heat	С	Mn	Р	S	Si	Ni	Cr	Мо	Cu	v
				SA	508 C12					
BBB ^a	0.22	0.64	0.007	0.014	0.28	0.68	0.34	0.58	0.02	0.022
15812 ^b	0.20	0.76	0.005	0.021	0.27	0.78	0.38	0.62	•••	0.041
125H601°	0.21	0.61	0.011	0.015	0.25	0.76	0.38	0.65		0.01
				SA	533 B-1					
BCR	0.23	1.40	0.005	0.004	0.25	0.70	с	0.57	с	с
BH	0.19	1.28	0.009	0.013	0.25	0.61	0.04	0.55	0.200	0.004
CEB	0.21	1.35	0.009	0.021	0.25	0.55	0.03	0.48	0.120	0.003
BCP	0.23	1.33	0.011	0.025	0.23	0.66	c	0.48	0.26	c

TABLE 2-Chemical analysis (percent by weight).

^a Nozzle cutout.

^b Outlet nozzle.

^c Not reported.

Heat	Yield Strength, MPa	Ultimate Tensile Strength, MPa	Elongation, % in 50 mm	Reduction of Area, %
		SA508 C12		
BBB	487.8	624.9	26.5	68.7
15812	466.0	590.0	27.0	56.2
125H601	435.0	598.0	26.0	69.9
		SA533 B-1		
BCR	496.1	641.0	24.0	
BH	449.0	595.0	27.0	65.0
CEB	434.1	584.3	26.5	65.0
BCP	444.8	600.0	28.0	66.0

TABLE 3—Room temperature tensile properties.

Test Results

The experimental results obtained on a high (0.025%) sulfur material tested in a 288°C BWR environment are presented in Figs. 1 through 3.

Figure 1 presents the results in the conventional format of crack growth rate versus applied ΔK . Included in this figure are the flaw growth reference curves from Section XI, Appendix A, of the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code. The data presented appear to scatter widely within the range outlined by the ASME curves. There are a few data points above the curves and no points on the ASME air line.



FIG. 1—Crack growth rate results for experiments conducted on SA533 B-1 material with 0.025% sulfur in 288°C BWR environment.



FIG. 2—Crack growth rate as a function of loading frequency for 0.025% sulfur SA533 B-1 in 288°C BWR environment.

These results are fairly typical for material/environment conditions in which EAC is observed. Carefully examining the data points indicates that there is a trend to the apparent scatter. The data vary as a function of the loading frequency.

The same data shown in Fig. 1 are plotted in Fig. 2. This time, the crack growth rate is plotted as a function of the loading frequency. The trend in growth rate as a function of frequency is easily seen. The data pairs with the arrows connecting them represent results in which the measured crack growth rates were not constant with time. In these experiments, the crack started moving at one rate and then changed to a second rate. The arrow represents the direction in which the crack growth rate increases until a maximum is reached. At some low loading frequency, the high crack growth rate cannot be maintained and the crack growth rate slows to some lower value. The mechanistic explanation for this is discussed later.

Figure 3 represents a third way of presenting these same test results. Here the crack growth rates are plotted as a function of time, rather than cycles, as was done in the two previous figures. In this figure, the crack growth rate measured in the experiment has been multiplied by the loading frequency to obtain the rate in terms of time. This value is plotted versus the crack growth rate predicted for this ΔK level and R ratio for an inert environment. The inert-environment rate was obtained from best-fit line to crack growth rate data obtained in air for a number of heats of the pressure vessel material tested in this program. The measured air crack growth rates from this project differ from that recommended by the ASME curves. With this type of data presentation, the results fall in a relatively tight band. The transient information is still represented by two data points joined by an arrow. These transients all occur at about the same inert environment growth rate.



FIG. 3—Fatigue crack growth rates plotted in time-based format for 0.025% sulfur SA533 B-1 in 288°C BWR environment.

This time-based presentation was originally suggested by Shoji [15] and is based on the concept that the crack tip strain rate is directly proportional to the inert crack growth rate. Using this hypothesis, there is a range in crack tip strain rates over which EAC occurs. Also, Fig. 3 shows that the time-based crack growth rate over this range in strain rates is nearly constant at a value of from 2 to 5×10^{-8} m/s. This method of data presentation appears to hold promise for future application of this type of data.

Figure 4 presents the data from the experiments conducted in a BWR environment on the lowest sulfur material tested, a heat of SA533 material with 0.004% sulfur. These results show no environmental effect on the crack growth rates. In this case, the data fall on the inert-environment line. Figure 5 presents a similar result obtained in a 288°C PWR environment on a heat of SA508 material with a measured sulfur content of 0.012%.

The results shown in Fig. 6 were obtained on a heat of SA508 material, which had the highest sulfur content of the SA508 heats tested. In this example, the results are from experiments performed in a 288°C PWR environment. These results show a similar trend to those of the high-sulfur heat of SA533 in Fig. 3 but with a slightly lower crack growth rate (due to EAC) and a narrower range in strain rates over which EAC is observed.

In Fig. 7, this same material tested in a 288°C BWR environment shows a response closer to that shown in Fig. 3.

Figure 8 presents a summary of all the results from this program in the time-based format. The experimental results in the BWR environment all fall either on the air line or, in those tests in which EAC was observed, in a relatively tight group. The results in the PWR environment are not so well behaved.



FIG. 4—Crack growth rate plotted in time-based format for 0.004% sulfur SA533 B-1 in 288°C BWR environment.



FIG. 5—Crack growth rate plotted in time-based format for 0.012% sulfur SA508-2 in 288°C PWR environment.



FIG. 6—Crack growth rate plotted in time-based format for 0.021% sulfur SA508 Cl2 in 288°C PWR environment.

The results from two of the four materials that showed EAC in a PWR environment fall in the same band developed by the BWR results, while two of the materials produced intermediate results. In these two cases, the strain rate region over which EAC was observed was reduced. The EAC was not observed in the lower strain rate region defined by the other materials. A curious aspect about these observed results is that they were generated on two tested materials that had higher bulk sulfur levels. This observation led to work on attempting to quantify the sulfur morphology of the test materials.

Quantitative scanning-electron microscopy (SEM) was performed on each of the test materials to determine the size distribution of inclusion. Manganese sulfide inclusions of Type II were found to be the dominant inclusions. The results of this study can be seen in Figs. 9 and 10. The computer code used in this work counted the number of particles in each of five size categories assigned by the operator (Fig. 9). The four materials that exhibited a large amount of EAC are clearly different from the other three materials in this presentation. However, the difference among SA533 materials with 0.013, 0.021, and 0.025% sulfur is too small to explain the difference in behavior as seen in Fig. 8.

Figure 10 plots the bulk sulfur content versus the area fraction of MnS particles. Here there is a clear demarcation between those materials susceptible to EAC and those that are not. Again, a clear difference between the three SA533 materials in which EAC was observed is not shown. Apparently, a more sophisticated technique is needed if further separation is desired in the quantification of sulfur morphology.

The data presented in Figs. 1 through 8 were all generated in constant- ΔK experiments



FIG. 7—Crack growth rate plotted in time-based format for 0.021% sulfur SA508 Cl2 in 288°C BWR environment.

where the frequency was decreased between individual experiments. The time-based plots were always generated from right to left. However, four experiments have been conducted in which the frequency was increased after the completion of a series of frequency-decreasing experiments to determine if hysteresis exists. There is a critical sulfur content at the crack tip theory, proposed by Combrade [16], which predicts that there is a critical crack growth rate needed in order to sustain EAC. If the growth rate drops below this value, it is necessary for the mechanical growth rate to be increased above this rate for EAC to occur. The experiments, the results of which are presented in Figs. 11 and 12, were planned to confirm this theory.

Figure 11 shows the crack length versus cycles information generated in one of these frequency increasing experiments conducted at a ΔK level of 66 MPa \sqrt{m} . In the far left of the figure, the data are the end of a previous experiment at a frequency of 0.0005 Hz. At this frequency, the crack is running relatively fast. When the frequency is decreased to 0.0001 Hz, the crack continues to run at the high rate for almost 100 cycles and 3 mm of crack extension but then slows to a lower crack growth rate for the next 300 cycles. The frequency was then returned to the original 0.0005 Hz, and the crack continued growing at the low rate for approximately 400 cycles and then the rate increased again to the high rate. These results are presented in the time-based format in Fig. 12.

The experiment was conducted twice at the ΔK level of 66 MPa \sqrt{m} . The other data points close to the air line in the region where EAC is evident represent the two earlier frequency-increasing experiments in which EAC did not occur. These experiments were



FIG. 8—Summary of time-based results for both 288°C PWR and BWR environments.



FIG. 9-Number of MnS inclusions versus percent of sulfur.



FIG. 10-Plot of MnS inclusions/cm² versus percent of sulfur in SA508 Cl2 and SA533 B-1.



FIG. 11—Results from fatigue crack growth experiments in which the loading frequency was increased and decreased.



FIG. 12—Crack growth rate plotted in time-based format for 0.013% sulfur SA533 B-1 in 288°C PWR environment.

conducted at ΔK levels of 22 and 44 MPa \sqrt{m} . In the cases of the two points in the region of the inert-environment growth rate of 10^{-9} , the crack grew from 1 to 1.5 mm during these experiments. In the next two experiments at the higher ΔK level, the crack grew more than 3 mm. We do not know if the rate would have increased at these ΔK levels if the crack had been grown a greater distance.

Since the sulfur content in the material appears to be the controlling variable, a series of experiments were conducted on a low-sulfur material (0.004% sulfur SA533) to determine if other sources of sulfur can cause EAC. In these experiments, various compounds of sulfur were first introduced into the autoclave environment and their effects determined on fatigue crack growth rate. Figure 13 presents the results of these experiments. This figure plots crack length versus cycles of these experiments. Sodium sulfide, sodium sulfate, sodium sulfate + oxygen, and sulfuric acid were all introduced into the autoclave in concentrations between 1 to 10 ppm with no measurable effect on the crack growth rate.

A second series of experiments was then conducted in which the sulfur was introduced directly into the crack. These experiments used the specimen shown in Fig. 14. A hole was placed in the back of the specimen so that the plane of the crack would intersect the hole. The PWR water chemistry contaminated with various concentrations of hydrogen sulfide (H_2S) was pumped through the crack at a flow rate of 2 mL/h. Two series of experiments were completed using this test procedure; results are presented in Figs. 15 through 18. The test conditions for each of the data points are presented in the figure.

In Fig. 15, H₂S concentrations of 500 and 50 ppm were evaluated. The numbers associated with each point represent the order in which the experiments were performed. Crack growth



FIG. 13—Effect of adding sulfur to 288°C PWR environment and crack growth rate of 0.004% sulfur SA533 B-1 at $\Delta K = 20$ MPa \sqrt{m} , R = 0.7, and f = 0.01 Hz.



FIG. 14—Schematic of specimen used in experiments injecting H_2S into tip of crack.



FIG. 15—Results from a series of fatigue crack growth experiments in which H_2S -contaminated PWR water was injected at the crack tip.

was started before the contamination was introduced. When the H_2S was introduced into the crack, the growth rate immediately increased to rates similar to previous tests in which EAC was observed. Removal of the H_2S from the inlet water to the crack tip did not cause the growth rate to decrease. The sulfur in the crack had to be removed by cleaning with hydrogen peroxide to eliminate the EAC. This same response was observed at a sulfur contamination level of 50 ppm. The time-based presentation of these data is shown in Fig. 16. Crack growth rates similar to those presented in Fig. 8 were observed, except for the extremely low frequency data in which the crack growth rate did not return to the air rate in the 0.00025-Hz tests.

A second specimen of the same 0.004% sulfur SA533 material was tested at significantly lower levels of sulfur contamination to determine the critical level of sulfur required for EAC. The results from these experiments are in Figs. 17 and 18. Points 1 to 4 were obtained with H₂S contamination of 3 ppm in the crack tip. (In these figures, the number associated with each point represents the order in which the experiments were conducted.) Experiment 2, the first experiment at a ΔK level of 6 MPa \sqrt{m} , did not show EAC, while Experiment 4 did. Experiments 2, 3, and 4 were conducted to determine if the ΔK threshold that has been observed for EAC was related to the availability of sulfur at the crack tip. Experiments 3 and 4 show that with enough sulfur available at the crack tip, EAC can be obtained at ΔK levels below the observed thresholds. The low rates measured in Experiments 8 and 9 appear to have been caused by more aggressive cleaning with hydrogen peroxide than was done in the earlier experiment. In this case, the specimen was cleaned with 38 ppm hydrogen peroxide (H₂O₂) in the crack at 66°C for 94 h. In the earlier case, the cleaning was done



FIG. 16—Results plotted in time-based format from a series of experiments in which H_2 S-contaminated PWR water was injected at the crack tip.



FIG. 17—Results from a second series of fatigue crack growth experiments in which H_2 S-contaminated water was injected at the crack tip.



FIG. 18—Results plotted in time-based format from a second series of experiments in which H_2S -contaminated PWR water was injected at the crack tip.

with 15 ppm H₂O₂ at 66°C for 52 h. It was necessary to move the crack 3 mm away from the cleaned region before EAC was again observed. The EAC was observed with both 3 ppm and 7 to 8 ppm H₂S and at ΔK levels of 7.7, 9, and 33 MPa \sqrt{m} .

The series of Experiments 11, 12, and 13 is of particular interest. In Experiment 11, the specimen was fatigued for 1000 cycles at 0.001 Hz after it had been cleaned with H_2O_2 and with 1 to 3 ppm H_2S contamination. It showed no evidence of EAC. Although the crack growth was less than 1 mm under these conditions, the elapsed time was more than 11 days. At this point, the level of sulfur contamination was increased to 7 to 9 ppm. The crack growth rate then increased to that shown as Point 12. The contamination was then removed from the water being supplied to the crack tip and the growth rate decreased back to the rate represented by Point 13. This represents the first time that EAC had been induced by adding H_2S and then eliminated by removing the H_2S from the PWR water supplied to the crack tip.

Figure 18 is this same information plotted in the time-based format. The information on this plot is similar to that seen in the other time-based plots. No attempts were made in the experiments presented in this figure to go outside the envelope or data developed for the SA533 and SA508 materials. Experiments 3 and 4 are two points that were measured at extremely low ΔK levels at which EAC had not been previously observed. With the sulfur present at the crack tip by artificial means, these results fall in line with the other results where EAC is present.

Discussion of Results

From the information obtained on the seven heats of material tested in this program, some observations can be made as to the susceptibility to EAC versus sulfur content. The three heats of steel with sulfur content of 0.020% and above were all susceptible to EAC in both the PWR and the BWR environments. Of the three heats with sulfur content between 0.01 and 0.02%, one was susceptible to EAC while the other two were not. The one low-sulfur heat tested was not susceptible.

From the quantitative metallographic work, it appears that the number of MnS particles in the 5 to 10 μ m range (and perhaps from 10 to 15 μ m) is important in determining susceptibility to EAC. This observation of the important size range appears to agree with that made by Bulloch [17]. However, he also observed the need for clusters of sulfide inclusions. The metallography performed in this project did not include a study of the presence of clusters.

From these two observations, it appears possible to establish an accurate screening procedure to catalog materials on their susceptibility to EAC based on chemical composition of the material and on quantitative metallography. This could be useful in evaluating old structures and in ordering material for new ones.

A significant effect of prior history has been observed in the experimental data just reported. Examples of this effect were observed when the high crack growth rates associated with EAC could not be sustained in frequency-decreasing experiments below some frequency level and when frequency-increasing experiments either do not attain the same high growth rates or do so only after substantial delays. These effects of history can have a significant impact on the results and interpretation of results of fatigue crack growth experiments conducted in aggressive environments.

Most fatigue crack growth rate experiments are conducted under constant-load conditions rather than constant- ΔK conditions used in this program. These experiments are usually started at ΔK levels and loading frequencies that fall within the envelope of conditions in which EAC will exist. In effect, these are the same conditions that exist in the constant- ΔK , frequency-increasing experiment. This means that a significant amount of either time or crack growth is needed before EAC will develop. During this period, the crack will be extending at some rate between the air rate and the EAC rate, and the ΔK level will be increasing. After sufficient crack extension, the full EAC rate will be realized.

From the test results described earlier, we know this process will follow a different path, depending on the starting ΔK level and loading frequency. From other data [18], it appears that it is also a function of the R ratio of the loading. These history effects account for the two slopes to the ASME fatigue crack growth reference curves.

More frequency-increasing, constant- ΔK experiments should be performed to fully characterize the impact of these history effects.

From the experiments in which H_2S -contaminated water was introduced directly at the crack tip, it appears that the Combrade's model [16] of critical sulfur content at the crack is at least partially correct. The critical sulfur level is between 1 and 10 ppm based on these results. The EAC occurs at these levels, but the high growth rates do not occur as soon as the sulfur is made available. There are transient periods; also, the process is reversible. If the H_2S is removed, the EAC is removed but, again, through a transition period. These transition periods cannot now be explained by Combrade's model. There is some mechanism in which the sulfur at the crack tip is stored for future use or accumulated to achieve the critical level.

There are a number of chemical reactions occurring at the crack tip. The formation of iron oxide, iron sulfide, and lithium sulfide are some of the more important ones. The thermodynamics of these reactions have to be evaluated to determine what is most likely to happen at the crack tip.

Combrade's model can be used to predict the time-based results obtained in this project. There are a number of time-dependent processes going on as the crack tip advances. Aside from the crack growth itself, these include:

- 1. Dissolving of the MnS particles as they are exposed.
- 2. Exchange of the crack tip water with the bulk water by both pumping due to the fatigue cycling and the external fluid flow.
- 3. Diffusion.

As the loading frequency is decreased, a point is reached where the processes removing sulfur from the crack tip are operating faster than new particles are being exposed and dissolved. When this happens, the crack growth rate drops dramatically to values near the air rate. This explanation is consistent with the data presented in this report and the effect of flow rate information reported by Scott [19].

Conclusions

A number of conclusions have been reached based on the results of this research.

- 1. The sulfur content and the sulfur morphology are the most important variables to determine susceptibility of a material to EAC.
- 2. The time-based method of data interpretation is very useful in analyzing the data. This format will simplify the engineering use of the data.
- 3. A number of effects of prior history are present in fatigue crack growth information in which EAC is present. This must be taken into account when using the data to prevent erroneous conclusions.
- 4. The model based on critical sulfur level at the crack tip for the observed EAC appears to be essentially correct. An addition to the model that includes a method of accumulating the critical level over time appears to be needed to explain some of the experimental results.

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Interactive Effects of Cold Work, Yield Strength, and Temperature on Sulfide Stress Cracking

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ABSTRACT: In an effort to better define the interactions among cold work, yield strength, and temperature with respect to sulfide stress cracking (SSC), a statistically designed experiment was conducted using a 90 grade, sour service, low-alloy tubular steel. The SSC tests were conducted using stressed, notched, bent beam specimens exposed to the National Association of Corrosion Engineers (NACE) solution at various temperatures. The experimental strategy was based on a face-centered cube design, and regression analyses were used for interpretation of the data. Results indicated that the primary influences on SSC were those of yield strength and temperature and that cold work had little effect up to a prestrain of 5%. The threshold stress for a given yield strength was found to change with temperature.

KEY WORDS: fatigue (materials), cracking, environmental effects, stress corrosion cracking, sulfide stress cracking, stress corrosion tests, cold working, hydrogen sulfide, temperature, alloy steels

The search for fossil fuel-based energy sources in recent decades has served to spur a significant growth in the exploitation of deep and ultra deep oil and gas reservoirs. Well depths of 4572 to 6096 m (15 000 to 20 000 ft) are no longer uncommon. Additionally, the offshore industry is on the threshold of a new era in deep water development, especially in view of the viability of novel technology such as the tension leg platform [1].

A common problem shared by deep oil and gas reservoirs onshore and offshore is the selection of materials for production and completion equipment that will combat the harsh environmental conditions downhole. The occurrence of high-temperature and high-pressure "sour" oil and gas reservoirs containing corrosive species such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S) is common even for moderate water depths offshore in the Gulf of Mexico, North Sea, Middle East, and Far East [2]. To further complicate offshore production, waterfloods used to maintain reservoir pressure will cause a "sweet" reservoir to become sour due to H_2S produced by anaerobic bacteria.

Sulfide stress cracking (SSC) is a catastrophic failure phenomenon [3] that can occur in steels and alloys in the presence of H_2S , given the proper combination of environmental

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conditions. Much has been written about the effects of H_2S on cracking of steels [4,5], and concerted efforts on the part of interested parties has led to the development of the National Association of Corrosion Engineers (NACE) Specification, MR-01-75 [6]. It is easy to understand the safety and economic importance of SSC prevention when the consequences of catastrophic failure of tubulars and well control equipment are considered [3].

The SSC in oil country tubular goods (OCTG) made from carbon/low-alloy steels is influenced by a host of material and environmental variables on which several reviews of laboratory and field data expound [4,5,7]. According to these reviews, the variables, cold work, yield strength, and service temperature are considered to have the most pronounced effect on the stress level at which SCC occurs.

The threshold stress for inducing SCC in steels has been shown to be inversely proportional to the yield strength of the material [4,7-9]. This, coupled with higher design loads, especially for deep wells, has led the industry to develop and apply sour grade C-90 grade tubulars (90 000 psi (620 MPa) minimum yield strength) for deep-well, high-stress applications. The C-90 tubulars represent the upper limit for SSC prevention at all service temperatures in carbon/low-alloy steels [5,7]. The increasing development of deeper reservoirs pushes the limits of strength levels that can be safely used in high-pressure H₂S environments. Development is now under way for providing the industry with low-alloy, sour service grades exceeding the strength levels of C-90 [10,11]; however, threshold stresses are expected to decrease accordingly.

The influence of service temperatures on SSC is well known, and it is thought that at temperatures exceeding 65.6°C (150°F), SSC is normally of minor concern [4,5,7]. This phenomenon, akin to hydrogen embrittlement of high-strength steels [12], has been exploited in the use of P-110 and V-150 grades for lower zones in deep wells where temperatures are consistently above 65.6°C (150°F).

One of the most poorly understood variables with regard to SSC is cold work, although the currently held belief is that cold work will always reduce the threshold stress for lowalloy steels. It is no surprise, therefore, that much of the literature data on the subject is contradictory and confusing. Treseder and Swanson [13], in a study on X-52 pipeline material and J-55 and C-75 OCTG, showed that increasing cold work was prone to lowering of the threshold stress for SSC. The limits of acceptability of threshold stress indicated that J-55 and X-52 tolerated moderate levels of cold work (up to 15% reduction in area), while C-75 only tolerated 5% cold work. Dvoracek [8] showed a reduction of 40% in critical stress for SSC as a result of cold working. Contrastingly, a study on sulfide corrosion fatigue by Bellow and Faulkner [14] indicated that the endurance limit for cold worked threads is higher than that of simple machined threads. Their study also showed that the morphology of SSC in cold worked material is different from that of simple machined specimens wherein the former exhibited sharp-bottomed notches rather than rounded pits. Levesque [15] maintains that the maximum reduction in threshold stress for SSC in NACE tension tests is up to a plastic strain of 1% and beyond that cold work has no effect. This result contradicts earlier data [8, 13] that indicate a gradual reduction in SSC threshold stress with increasing cold work. Some of the contradictory results could possibly be clarified if the nature of the cold work was known. Not all references are specific as to this aspect.

The standards that address cold work are also not in total agreement with regard to SSC. American Petroleum Institute (API) Specification 5AC states the following in Section 2.2: "Grade C-75 and L-80 pipe shall not be subjected to cold working after the final tempering treatment, except for that which is incidental to normal straightening operations . . ." while the NACE Specification MR-01-75 [6] allows up to 5% extreme fiber deformation for carbon and low-alloy steels with the exception of chromium-molybdenum (Cr-Mo) steels. Cold deformation of the Cr-Mo steels (AISI 41XX and modifications) is not permitted by MR- 01-75. These steels are the candidate materials for tubular grades such as C-90. Considering that the yield strengths for C-75, L-80, and C-90 overlap, it is apparent that a uniform criterion is not applied regarding acceptance levels for cold work.

Analyses of field failures have also been used to caution the user against cold work [4, 16]. In a compilation of field failures [16], hardness values associated with cold rotary straightening and deep tong marks in C-75 tubing have been shown to be in the vicinity of RC 40. In the same compilation, manganese-rich bands in C-75 possessed comparable hardness levels and were also susceptible to cracking. Considering that normalized and tempered steels do not strain harden appreciably [14], it is not clear that cold work alone caused excessive localized hardening or that hardness alone can explain the effects of cold work.

The lack of consistency in the literature indicates the need for a systematic study on the effect of cold work on SSC. Given that yield strength increases accompany cold work and that data for quenched and tempered grades such as L-80 and C-90 are not available, such a study should be conducted as a function of yield strength.

It is common for the previously mentioned studies to be conducted on the basis of "one parameter at a time." This is done primarily for ease of data interpretation. However, this method does not address the combined effects as well as interactions of the variables. Statistical design of experiments [17,18] offers the means for deriving and analyzing data from multiparametric systems. These data analyses offer the advantages of providing more realistic material/system behavior and interactions among parameters.

This paper describes the experimental design, results, and analyses of a rigorous program designed to investigate the effects of cold work (tensile elongation), stress level, and temperature on sulfide stress cracking. The combined effects and interactions of the three parameters are described as well as the implication of the results with regard to straightening at room temperature, temperatures affecting SSC, and localized damage such as tong marks.

Statistical Experimental Design

Experimental design progresses through several stages from the inception of an experiment to its completion. Recognizing these stages and properly developing each stage can transform a series of observations into a predictive model.

The first stage in an experimental program is to screen the candidate independent variables. The screening may take the form of a checklist whereby through experience, discussion, literature, etc., certain variables can be eliminated, that is, held constant at a predetermined level. Screening can also be done by statistical means where up to 30 candidate variables may be experimentally examined to determine which are first-order factors. In this study, the three variables chosen were cold work, temperature, and yield strength for reasons outlined earlier.

The next stage involves the development of an experimental region where the response is to be explored. To define this region, a basic or average value for each independent variable was selected. The variation interval was chosen symmetrically above and below the basic or mean level. The upper and lower levels thus obtained were coded +1 and -1, respectively. The basic level was coded 0. These codes were used to develop a symmetrical test matrix that outlines the experimental region of interest.

Once the experiments were completed, thus providing data for each of the responses of interest (dependent variables), empirical models were developed. An empirical model is useful for interpolation. Extrapolation beyond the experimental ranges may be attempted, but modeling outside the region must be confirmed by experimental results. The face-centered cube (FCC) design was chosen since the variables were expected to produce significant response surface curvature [7]. This design model is shown in Fig. 1. The FCC



FIG. 1—Conceptual drawing of a face-centered-cubic design. The experiments include each corner of the cube, the center of each face, and the center of the cube.

design strategy allows definition of response surface curvature using regression analyses to define the response surfaces. Once the design was finalized, the actual test matrix could be encoded. The ranges investigated for the independent variables screened by this series of experiments and their factor coding are listed in Table 1.

The face-centered cube test matrix is shown in Table 2. The pattern was developed by systematically varying X_1 , X_2 , and X_3 over the high, basic, and low values for the factors given in Table 1. The trial numbers were added for convenience. Each trial number corresponds to a location indicated in Fig. 1. The test sequence was randomly generated from the design pattern to eliminate bias errors. The experiments included four replicates to measure experimental precision.

The results of the tests are the "Y" or the response value, namely, threshold stress for the SSC tests. Determining the threshold stress was not a straightforward calculation since it is a discrete value determined from a series of tests at incremental stress levels. One of the historically [19] accepted methods for determining threshold stress uses 10 to 12 specimens stressed at increasing intervals of 10% of the yield strength. In the case where two samples failed and one did not fail in successive samples, a probit analysis historically has been used to determine the threshold [19]. For the current series of experiments, it was decided to take a similar but more efficient approach to determine the threshold. Three

Factors		- 1	0	+1
$\begin{array}{c} X_1 \\ X_2 \\ X_3 \\ Y \end{array}$	cold work, % temperature, °C yield strength, ksi ^a threshold stress, ksi	0 20 87.2	2.5 55 95.3 response	5 90 99.1

TABLE 1—Factor coding.

^a The yield strength of the test material was varied by heat treatment, thus the alloy composition was not a variable.

Trial			X ₃ Yield Strength		Y Threshold Stress		
	$X_1,$ % cold worked	X_2 temperature, °C	MPa	ksi	MPa	ksi	
1	0		600	87.2	827	120	
2	5	20	600	87.2	779^{a}	113^{a}	
3	0	90	600	87.2	779 ^a	113 ^a	
4	5	90	600	87.2	779," 779 ^a	113, ^a 113 ^a	
Factorials							
5	0	20	683	99.1	738	107	
6	5	20	683	99.1	738	107	
7	0	90	683	99.1	890, ^a 890 ^a	129, ^a 129 ^a	
8	5	90	683	99.1	890, ^a 890 ^a	129, ^a 129 ^a	
9 (center point)	2.5	55	657	95.3	855, ^a 855, ^a 855 ^a	124, ^a 124, ^a 124 ^a	
10	0	55	657	95.3	855ª	124"	
11	5	55	657	95.3	855ª	124"	
12	2.5	20	657	95.3	910	132	
Star points							
13	2.5	90	657	95.3	855ª	124 ^{<i>a</i>}	
14	2.5	55	600	87.2	779ª	113ª	
15	2.5	55	683	99.1	890 ^a	129"	

TABLE 2—Face-centered cube test matrix.

^a Calculation based on threshold stress being equivalent to the highest level of applied stress.

samples were tested at each of four different stress levels (40, 70, 100, and 130% of the yield strength). By using this technique, the stress range of interest was adequately covered and the impact of each individual specimen on the overall results was reduced. With single specimens tested at 10% increments, the impact of each sample on the overall results was significant. Whereas by testing three samples at each stress level, the results of each sample were tempered by the other two, thus avoiding a skew in the results from one data point. Thus, an analysis similar to a probit analysis can be used to yield a much improved degree of precision. The analysis was based on a 50% survival rate. Any probability of survival could be selected, but 50% is historically accepted for threshold stress calculations [13,19]. Figure 2 shows a graphical example of a threshold calculation.

Experimental Procedure

The material used for this test was a quenched and tempered C-90 grade steel tubular having a 177.8 mm (7-in.) outside diameter and a 19.05 mm (0.75-in.) wall thickness. The chemical analysis is shown in Table 3.

Several 406.40-mm (16-in.) long sections were cut from the original length of pipe. These sections were tempered to achieve the range of yield strengths shown in Table 4. After heat treating was completed, the sections were machined into long rectangular bars. The raw stock for the cold-worked material was obtained by prestraining the bars to the specified levels, that is 2.5 and 5%. The prestrain was imparted by uniform elongation through axial loading. Gage sections of 51 mm (2 in.) were marked along the length of the 400 by 38 by 13-mm bar. The bars were slowly elongated, and between each increment the gage distance was measured with a vertical cathetometer to determine the amount of elongation and the uniformity throughout the length of the bar. The bars were elongated slightly beyond the calculated values to account for the elastic portion of the total strain.



FIG. 2—Example of a threshold stress calculation for the three different outcomes that were observed. If failure did not occur at 130% of the yield strength, that stress was taken as the threshold.

After prestraining, notched tested bars were machined from the mid-wall into test specimens with the dimensions shown in Fig. 3. The V-notch was oriented perpendicular to the radius of the pipe.

The specimens were cleaned in acetone and stressed in a three-point bend system as shown in Fig. 3. The ends were supported across a 63.5-mm (2.5-in.) span. Stress was applied by advancing the loading screw until the deflection calculated from Eq 1 was attained.

$$D = \frac{\sigma L^2}{6Et} \tag{1}$$

where

E = Young's modulus: 20.7×10^4 MPa (30×10^6 psi),

- t = coupon thickness of 6.35 mm (0.250 in.),
- L = span of 63.5 mm (2.5 in.),
- D = deflection in mm, and
- σ = applied stress (MPa).

С	Mn	Р	S	Si	Cu	Ni	Cr	Мо	v	Nb	Al	Ti
0.31	0.87	0.013	0.002	0.27	Mil	L ANAI	YSIS	0.43			0.043	
0.51	0.07	0.015	0.002	0.27	 Indepei	ndent A	U.94 Analysi	0.45 (S			0.045	
0.37	0.92	0.014	0.004	0.30	0.01	0.09	1.02	0.43	0.008	0.016	0.067	0.15

TABLE 3—90 grade pipe chemical analysis.
	Yield Strength, aim	Yield S	trength, ual	Ter Stre	nsile ength		Hardness
MPa	ksi	MPa	ksi	MPa	ksi	% Elongation	HRC
690 655 600	100 (as received) 95 (740°C HT) ^a 87 (750°C HT)	683 657 601	99.1 95.3 87.2	756 707 678	109.6 102.5 98.4	26 25.3 26.5	21 20 19

TABLE 4—Yield strength range investigated.

^a Heat treatment temperature.

Each test involved submerging 12 stressed specimens in an H_2S saturated solution at a specific temperature for 100 h. The solution consisted of distilled water containing 5% sodium chloride and 0.5% glacial acetic acid.

After the coupons were placed in the solution, the solution was purged with nitrogen for approximately 1 h to remove oxygen. During this purge, the solution was heated to the test temperature. At the end of the purge, the H_2S was introduced. The solution was continually saturated with H_2S for the 100-h test duration. For each experimental combination, 12 coupons were stressed at four different levels (40, 70, 100, and 130% of the yield strength), three at each level. The various test parameters are shown in Table 2.

Results

The threshold stress (the Y or response value) that results in a 50% failure rate for each experimental combination was calculated as

$$\frac{\text{threshold stress} = (\text{yield strength}) \times (\% \text{ of yield strength resulting in 50\% failures})}{100}$$
(2)

A graphical method for determining the percentage of yield strength resulting in 50% failures is illustrated in Fig. 2. This figure shows the three different failure combinations that were observed for the three specimens that were tested at each load level. Line 1 represents no failures at 40 and 70% of the yield strength, one failure at 100%, and three failures at 130%. Line 2 represents no failure at 40, 70, and 100% and three failures at 130%. Line 3 represents no failures at 40, 70, 100, and 130%.

Only four of the fifteen trials had specimens that failed. All specimens that failed, cracked at the notch. A typical fracture surface is shown in Fig. 4. While it is not an ideal experimental situation to have specimens that did not fail, this is not untypical for threshold stress experiments [19]. Usually in this situation, the highest stress level is defined as the threshold. In this analysis, it was conservatively assumed that when no failures occurred at 130% of the yield strength, then that stress was the threshold. Additional tests at 160% of the yield strength confirmed that 130% was a conservative threshold estimate.

The threshold stresses calculated from Eq 2 are shown in Table 2 and plotted in Fig. 5. Figure 5 shows the experimental combinations with the threshold stress (MPa) results superimposed for the eight "corners" of the experimental region and the overall centroid. Plotting the data in this manner is useful for determining rough estimates of the independent variable effects. Two important results are noted from Fig. 5:

- 1. percent cold work appears to have little effect on threshold stress, and
- 2. temperature appears to have significant effects on threshold stress.











3 POINT BEND SPECIMEN DIMENSIONS

FIG. 3—Stressing fixture and specimen dimensions.



FIG. 4—The SSC fracture surface for a specimen with zero cold work loaded to 130% of the yield strength and tested at 20°C.



FIG. 5—Experimentally determined threshold stresses superimposed on the experimental region.

Figures 6 and 7 are raw data plots of threshold stress versus temperature and yield strength, respectively. In looking at these figures, one must keep in mind that the other experimental variables are changing. For example, Fig. 6 shows threshold stress plotted versus temperature; however, both the cold work and yield strength variables are varying at three different levels in this plot. The same analogy applies to Fig. 7. A regression analysis was used to assess the joint effect of cold work, temperature, and yield strength on threshold stress. Over the experimental region, temperature and yield strength were important in explaining threshold stress; the percent of cold work was found not to influence the threshold stress (confirming what was indicated by Fig. 5). The regression model can be written as

Predicted threshold stress = 126 + 2.99 [(T - 60.3)/28.4]+ $0.84 [(\sigma/6.895 - 94.2)/4.98]$ (3) + $3.77 [(T - 60.3)/28.4] [(\sigma/6.895 - 94.2)/4.98]$ - $5.32 [(\sigma/6.895 - 94.2)/4.98]^2$

where

T = the service temperature (C), and

 σ = the yield strength (MPa).

Since the experimental variables have been centered and scaled by the parenthetical expressions in Eq 3, the magnitude of the regression coefficients indicate the relative importance of the different model terms in explaining threshold stress. All



FIG. 6—Plot of threshold stress versus temperature. Numbers in parenthesis indicate trial number.



FIG. 7—Plot of threshold stress versus yield strength. Numbers in parenthesis indicate trial number.

of the regression coefficients are statistically significant in the preceding model except for the linear yield strength term. However, since the square of the yield strength is in the model, the linear term was kept. Table 5 contains the details of the regression analysis.

Figure 8 is a contour plot showing the effect of temperature and yield strength on threshold stress over the experimental region. The contours of constant threshold stress show the features of the regression model described by Eq 3. The temperature by yield strength interaction effect on threshold stress is clearly seen; note that as temperature increases at a low yield strength, there is only a minimal increase in threshold, while the increase in threshold at higher yield strength is quite dramatic with only small increases in temperature. The linear, curvature, and interaction effects combine to give the highest predicted threshold stress (130 ksi) for the higher temperature and higher yield strength region. It is important to understand that the results can only be applied for the range of threshold stresses described by these experiments.

Discussion

The influence of cold work up to a prestrain of 5%, even when coupled with the stress concentration and plastic deformation associated with a notch, has been shown to have no influence on sulfide stress cracking of a high-strength steel. This finding appears to contradict the results of several investigations [8,13] and related field failures [4,16]. It is relevant to examine some of the current hypotheses to explain these apparent anomalies.

The cold-worked structure of a material depends upon the flow stress and is typically characterized by a series of cells where the walls are defined by dislocation tangles. This cell structure is usually well developed at strains of 10% [20]. The exact form of the cold-

Predictor	Coefficient	Standard Coefficient	t-Ratio	VIF"
Constant	125.922	2.036	61.84	
S-Temp [*]	2.989	1.101	2.72	1.0
S-YS ^c	0.843	1.458	0.58	1.8
T^*YS^d	3.765	0.998	3.77	1.0
YS**2 ^e	- 5.318	1.834	-2.90	1.8
S' = 4.729	$R^{2g} = 72\%$	$R^2 = 65\%$	•	
	AN	alysis of Variance		
Source	DF ^h	SSi	MS	F
Regression	4	872.55	218.14	9.8
Error	15	335.45	22.36	
Total	19	1208.00		
Row	Threshold Stress	Predicted	Fit	Residual
1	120	117.5		2.5
2	113	117.5		-4.5
3	113	111.8		1.2
4	113	111.8		1.2
5	113	111.8		1.2
6	107	112.1		-5.1
7	107	112.1		-5.1
8	129	128.6		0.4
9	129	128.6		0.4
10	129	128.6		0.4
11	129	128.6		0.4
12	124	125.1		-1.1
13	124	125.1		-1.1
14	124	125.1		-1.1
15	124	125.1		-1.1
16	124	125.1		-1.1
17	132	120.4		11.6
18	124	129.8		-5.8
19	113	114.6		-1.6
20	129	120.4		8.6

TABLE 5—Regression results.

^{*a*} VIF = variance inflation factor.

^h S-Temp = linear temperature term in regression equation.

 $^{\circ}$ S-YS = linear yield strength term.

 d T*YS = temperature and yield strength interaction term.

" YS^{**2} = yield strength squared term.

 ^{f}S = Regression standard deviation.

^s R^2 = coefficient of determination.

 h DF = degrees of freedom.

i SS = sum of squares

 j MS = mean square.

 $^{k}F = F$ -ratio.

worked structure depends on the material, the amount of strain, the strain rate, and the deformation temperature.

Alloying elements added to the material will increase the energy stored from the cold work and affect the material's response to environmental cracking. The amount of stored energy is dependent on the type of deformation process and the temperature of deformation. A lower temperature increases the stored energy while a slow strain rate decreases the stored



FIG. 8—A contour plot of the SSC data.

energy. The flow stress or the way a material responds to cold work is described by the following relationship [20].

$$\sigma_0 = \sigma_i + \alpha \ Gb\rho^{1/2} \tag{4}$$

where

- σ_0 = flow stress (yield strength),
- σ_i = friction stress opposing dislocation motion,
- α = a material numerical constant that varies from 0.3 to 0.6 for various metals,
- b =lattice spacing,
- G = shear modulus of elasticity, and
- ρ = dislocation density.

In Ref 8, the C-Mn steel (C-75) did not show a significant change in SSC resistance until the amount of cold work exceeded 8%. At these cold work levels, the strain hardening (stored energy) will increase the material hardness [13] and thus increase the flow stress, σ_0 , along with increasing the susceptibility to SSC. Up to 5% prestrain, no increase in hardness was detected in the current test series, and thus lower levels of cold work should not have a significant impact on material hardness or SSC resistance. Other experimental efforts, though effective in describing the impact of higher levels of cold work on SCC, have in actuality only been observing a yield strength effect that is dependent on the materials strain hardening behavior. Another important aspect of understanding any strain hardening phenomena is the backstress produced by cold deformation, better known as the Bauschinger Effect. A material strained beyond yield in a given direction will exhibit a lower friction stress opposing dislocation motion, σ_i , and similarly a lower flow stress, σ_0 , if loaded in the *opposite* direction. The Bauschinger Effect is applicable to cold-worked materials and may explain the susceptibility of low-strength steel to SSC after cold deformation. The lower flow stress after cold working would cause the applied stress as a percentage of yield strength to be higher than that calculated from the yield strength measured prior to the cold work. This would cause the results to be seemingly influenced by cold work, whereas in actuality the specimens were just more highly stressed. The Bauschinger Effect may be eliminated by a short duration stress relief at ~454 to 482°C (850 to 900°F).

Another potential means for SSC-related failures in cold-worked material stems from stress-induced phase transformations. Retained austenite may be present in quenched and tempered materials. This phase is unstable at room temperature and will transform to untempered martensite dependent on temperature changes or applied stress or both. Untempered martensite has a poor resistance to SSC [13] and thus a cold-worked area would exhibit a behavior similar to an improperly heat-treated alloy even though cold work had no other influence than to transform the retained austenite.

The pure yield strength effect, the Bauschinger Effect, and retained austenite are all probable influences on the outcome of previous cold work studies. The present work by no means completely quantifies the interactive effects of cold work, yield strength, and temperature, but does present a method by which further analyses of higher levels of cold work may be examined. This experimental method also eliminates the influence of the Bauschinger Effect since the prestrain was a tensile load and no compressive stresses were generated during specimen loading in three-point bending. Retained austenite is not a problem with this particular steel since the composition is designed to achieve 100% martensite upon quenching.

The implications of Eq 3 and Fig. 8 are that cold work up to a 5% prestrain will not influence SSC within the temperature and yield strength regions described by this experiment. Thus, cold straightening of fully-martensitic, sour-service tubular goods (that is, casing, tubing, drill pipe, etc.), possessing a yield strength of up to 689.49 MPa (100 ksi), is an acceptable practice provided the total plastic strain does not exceed 5% and the Bauschinger Effect is accounted for. Localized cold work such as that from glass bead peening, interference-type threads, metal-to-metal seals, etc., should not contribute to SSC, although sharp notches (tong marks, slip marks, etc.) may increase SSC susceptibility and the impact of the stress concentration must be considered. These results and the implications of this work should be reviewed by API and NACE in the light of excluding their limitations on cold work up to a prestrain of 5%.

At prestrain levels greater than 5%, the material's cold-work cell structure will develop further and increase the flow stress. This decreases a material's resistance to SSC as Treseder and Swanson [13] showed. But if the trends detected in this series of experiments extend to cold work levels greater than 5%, then the cold work will be a secondary effect to that of temperature. The experimental region above 5% cold work needs further testing before this effect can be resolved.

The temperature by yield strength interaction shown in Fig. 8 indicates that as temperature increases at a low yield strength, there is only a minimal increase in threshold while the increase in threshold at higher yield strength is quite dramatic with only small increases in temperature. This finding is consistent with the established sulfide film formation theory that at temperatures greater than 66°C (150°F), high-strength steels are more resistant to sulfide stress cracking [21] due to decreased hydrogen adsorption. The additional information generated by this study allows calculation of specific conditional threshold stresses that can

be compared to experimentally determined threshold values. This information will allow designers to generate information confirming selection of materials for downhole and surface applications.

Conclusions

- 1. The interactive effects of cold work, yield strength, and temperature on sulfide stress cracking (SSC) of a 90-grade, sour service tubular steel have been investigated using a statistically designed experiment. The results show that cold work, such as that induced by a 100-m temperature straightening operation, has no effect up to a prestrain of 5%. The threshold stress was found to be totally dependent upon the yield strength and temperature.
- 2. A model that describes how threshold stress varies with yield strength and temperature has been developed and shows the complex interaction between yield strength and temperature.
- 3. Cold work imparted to high-strength tubulars, when less than 5%, should not adversely affect a low-alloy, high-strength tubular steel.
- 4. Standardization bodies involved with specifications for these materials should consider these results in future revisions.

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Sensitivity to Sulfide-Stress Cracking at Welds in Line-Pipe Steels

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ABSTRACT: A metallurgical investigation was undertaken to identify the factors that are responsible for sensitivity to sulfide-stress cracking (SSC) in the heat-affected zone (HAZ) of microalloyed high-strength line-pipe steels, when the HAZ does not contain regions of high hardness. Sustained-load tests were conducted in the National Association of Corrosion Engineers (NACE) laboratory sour-gas environment to determine the regions in which SSC initiated, and thereby to identify which regions were most sensitive to SSC. In every steel studied, SSC initiated in a specific region of the HAZ, usually in the region that was heated into the intercritical temperature range during welding. One steel exhibited SSC sensitivity in the region adjacent to the weld metal, which was heated above the upper critical temperature during welding, and another steel exhibited SSC sensitivity in the base metal following a laboratory normalizing heat treatment. In all of the steels that were studied, the region that exhibited sensitivity to SSC contained columbium carbonitride precipitates that were coarser than those that were present in the pipe body, which was immune to SSC as fabricated. The only steel that did not fail in the SSC experiments was not alloyed with columbium. These observations suggest that sensitivity to SSC is related to the growth of columbium carbonitride precipitates from a size below 50 Å to a size ranging from 100 to 200 Å during welding or during some heat treatments. Thus, it should be possible to reduce sensitivity to SSC by modifying the chemical composition or the cooling rate from welding or both to suppress precipitate growth.

KEY WORDS: sulfide-stress cracking, pipe steel, weld heat-affected zone, columbium carbonitrides, fatigue (materials), cracking, environmental effects

On several occasions, failures have occurred in high-strength line pipe that is used to transport natural gas containing hydrogen sulfide (sour gas) [1]. The failures were associated with the double-submerged-arc seam weld. Laboratory experiments have duplicated such failures [2]. Cracking appeared to initiate in the weld heat-affected zone (HAZ), and often propagated through the weld, HAZ, and base metal. Although stepwise cracking also has been observed in the vicinity of the fracture, the failures have been attributed to sulfide-stress cracking (SSC). In most cases, the hardness of the HAZ and the weld metal was not substantially higher than that of the base metal, and in some cases the hardness actually was lower than the base-metal hardness. Thus, based on previous experience and the successful application of hardness-based guidelines, such as the empirically based criterion of acceptable performance in sour gas of steels with hardnesses no greater than 22 HRC [3], SSC was not expected in those pipes.

Because of the unexpected SSC failures that have occurred, the Pipeline Research Com-

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mittee of the American Gas Association initiated an investigation of SSC in the HAZ of welds in high-strength pipe. The objective of this research was to determine the features of the HAZ that result in sensitivity to SSC in high-strength line pipe, particularly for cases where the HAZ does not contain regions of high hardness. This paper describes the findings from that investigation. The research has shown that sensitivity to SSC in the HAZ is related to growth of columbium carbonitride precipitates in the HAZ during welding.

Research Conducted

Description of Pipes Studied

Most of the investigation involved studies of three high-strength microalloyed and controlled-rolled pipe steels. The pipes were made in accordance with API Specification 5L, with one pipe Grade X60 and the other two Grade X70. Selected experiments also were conducted with two lower strength steels, which were obtained from pipes that were produced according to ASTM Specification for Metal-Arc-Welded Steel Pipe for Use with High-Pressure Transmission Systems (A 381-81). Both of the lower strength pipes were Grade Y52, and were full-body normalized after welding. The chemical compositions of the steels are given in Table 1. One of the Y52 pipes, designated Y52N, was microalloyed with columbium and vanadium, whereas the other Y52 pipe, designated A-1, contained no columbium or molybdenum. All five pipes were produced with double-submerged arc seam welds.

Description of Weld Zones

The HAZ of the seam welds of the five pipes exhibited three principal microstructural regions, or subzones. Those subzones are shown for Pipe 1664 in Fig. 1, which presents a transverse metallographic section through a portion of the weld in the pipe. For identification, the subzones were numbered from 1 through 3, beginning with the subzone adjacent to the weld. The HAZs of the other two pipes were similar in appearance.

The three subzones of the HAZ were examined using optical and scanning-electron microscopy (SEM). Based on the microstructures present, it was concluded that material in Subzone 1 had been heated above the upper critical temperature (approximately 840 to 870°C), while material in Subzone 3 had been heated close to, but not above, the lower critical temperature (732°C). Material in Subzone 2 had been heated into the intercritical region between those two temperatures. None of the subzones in any of the pipe welds exhibited high hardness. Those data are shown in Table 2. The hardness data also show that the HAZ hardness for Pipes 1664, EA2, and A-1 were lower than, or equivalent to, the base-metal hardnesses, in most cases, whereas the HAZ hardnesses in Pipes and DY1 and Y52N were equal to or slightly higher than that of the base metal.

Dies					0	Chemica	al Comp	osition,	% by w	eight			
Identification	Grade	С	Mn	P	s	Si	Cb	v	Мо	Cr	Ni	Ti	В
1664	X60	0.08	1.52	0.009	0.012	0.07	0.034	0.000	0.19	0.025	0.09	0.000	0.0001
EA2	X70	0.07	1.54	0.016	0.008	0.24	0.026	0.064	0.05	0.170	0.09	0.001	0.0001
DY1	X70	0.07	1.69	0.017	0.005	0.34	0.055	0.079	0.29	0.014	0.31	0.013	0.0004
Y52N	Y52	0.12	1.22	0.012	0.006	0.26	0.047	0.054	0.049				
A-1	Y52	0.21	1.36	0.009	0.023	0.22	0.000	0.084	0.004	0.010	0.012	0.000	0.0002

TABLE 1—Compositions of pipes studied.

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FIG. 1—Three microstructural regions observed in the HAZ of Pipe 1664. Similar subzones were observed in the HAZs of the longitudinal seam welds in the other pipes studied.

As is shown in Fig. 2*a*, Subzone 1, which was closest to the weld, contained coarse-grained acicular ferrite adjacent to the weld, and finer-grained acicular ferrite farther from the weld. The acicular ferrite throughout that subzone contained cementite particles and fine, blocky islands of martensite or retained austenite or both, with dimensions of approximately 1 to 2 μ m. The martensite/retained austenite constituent has been observed in microalloyed and controlled-rolled steels by others, and often is referred to as M-A [4]. However, in the pipes that were studied in this investigation, very little of the M-A constituent was observed in the base metal. The microstructure of Subzone 2, shown in Fig. 2*b*, consisted primarily of polygonal ferrite with uniformly distributed patches of bainite or pearlite or both, and islands

D ' -	Average Hardness at Each Location in Weld Region ^a										
Pipe Identification	Weld Metal	Subzone 1	Subzone 2	Subzone 3	Base Metal						
1664	205 (91 HRB)	220 (94 HRB)	203 (90.5 HRB)	213 (92.5 HRB)	226 (95 HRB)						
EA2	248 (99.5 HRB)	223 (94.5 HRB)	204 (90.5 HRB)	214 (92.5 HRB)	222 (94 HRB)						
DY1	297 (28 HRC)	273 (24 HRC)	270 (23.5 HRC)	256 (21 HRC)	256 (21 HRC)						
Y52N	192 (88 HRB)	186 (85.5 HRB)	187 (87 HRB)	186 (86.5 HRB)	172 (83 HRB)						
A-1	201 (90 HRB)	197 (89 HRB)	202 (90 HRB)	196 (89 HRB)	194 (88.5 HRB)						

TABLE 2—Hardness measured in the vicinity of the seam weld.

^a Hardnesses measured with a Knoop diamond identer using a 500-g load. Rockwell B or C hardness conversions are reported in parentheses.



FIG. 2-Microstructures of HAZ Subzones 1 (a) and Subžone 2 (b) in Pipe 1664.

of the M-A constituent that were approximately 2 to 5 μ m in diameter. By scratching the M-A constituent and the matrix in Subzone 2 with a Knoop diamond indentor under a 1-g load, it was determined that the M-A constituent was substantially harder than the matrix; the higher hardness indicates that the M-A contained appreciable martensite. Subzone 3 was essentially a transition zone from Subzone 2 to the base metal, containing some fine, recrystallized grains.

Experiments Performed

Round-bar tension specimens with a 6.35-mm (0.25-in.) diameter reduced section were prepared from the pipes, with the weld region in the reduced section. The specimen axis

was oriented perpendicular to the pipe axis and centered approximately at the midwall. The reduced sections were not flattened. Some of the specimens from Pipe EA2 were given a normalizing heat treatment at 870°C, and some specimens from Pipe DY1 were given stress-relieving heat treatments at 480 and 700°C in laboratory furnaces before testing. Also, in some cases, low-temperature treatments in liquid nitrogen were employed before stress relieving the specimens from Pipe DY1, in an effort to transform the retained austenite in the M-A prior to applying a stress-relief heat treatment.

Sustained-load experiments were conducted in tension in a standard SSC environment, in accordance with the National Association of Corrosion Engineers (NACE) Standard TM-01-77, Testing of Metals for Resistance to Sulfide Stress Cracking at Ambient Temperatures. The runout time chosen was 300 h, and most specimens were removed from test after approximately that time if failure had not occurred.

Visual and metallographic examinations of the specimens were performed following the sustained-load expriments to determine the location of fracture initiation. This determination was based on observations of cracking and any surface blisters or stepwise cracks that were present in metallographic sections traversing the fracture region. In addition, some specimens from Pipe DY1 were tested using a closed-loop servohydraulic test machine, which was programmed to unload the specimen automatically when cracking initiated; the objective was to stop the test before the specimen was completely fractured. Cracking was detected by an increase in specimen compliance. The purpose of those experiments was to isolate the location of SSC initiation, and to verify initial observations that SSC initiated in a different subzone in Pipe C than in the other pipes.

The microstructures of the HAZ subzones that were determined to be sensitive to SSC were characterized by optical and scanning-electron microscopy, and were compared with other HAZ subzones and the base metal to identify features that contributed to SSC sensitivity. In some cases, additional microstructural analyses were performed by transmission-electron microscopy (TEM). Further metallurgical characterizations, including measuring the relative strengths of the subzones and residual-stress measurements by X-ray diffraction in each of the subzones, were conducted. The results of those characterizations were presented previously in a related paper [5].

Results

SSC Behavior

The influence of applied stress on the time to SSC failure for welds from the five pipes, determined with sustained-load experiments in the NACE sour-gas test environment, is presented in Fig. 3. That figure also presents data for specimens from Pipe EA2 in the laboratory-normalized condition and for specimens from Pipe DY1 in the laboratory-stress-relieved condition, with and without prior low-temperature treatments. In addition, data are presented for specimens that were prepared from the weld of a conventional X52 pipe that had a fully martensitic HAZ with high hardness (approximately 52 HRC), and that was adjacent to a joint of pipe that failed in sour-gas service. Other data from the technical literature also are included in the figure, for comparison [4].

Figure 3 demonstrates considerable scatter in the data from replicate experiments for a given pipe. Normalizing the applied stress as a percentage of yield strength did not reduce the scatter. Within that scatter, there does not appear to be any significant difference in SSC behavior among the pipes as received or with any of the heat treatments that were applied to reduce the sensitivity to SSC; the only exception is Pipe A-1, which did not fail in any of the tests.

For pipes that failed in the SSC tests, the present data are in reasonable agreement with



FIG. 3—Variation of time to failure with applied stress for specimens from the weld regions of several pipes exposed under load in the NACE SSC environment. Partially filled symbols represent specimens that were given stress-relief heat treatment, low temperature treatments, or normalizing treatments in an attempt to alter the SSC behavior. Horizontal arrows indicate that specimens did not fail.

those found in the technical literature, as shown in Fig. 3. More importantly, four of the pipes in the present study, which did not contain regions of high hardness in the HAZ, exhibited SSC behavior that was comparable to that of the X52 pipe, for which high hardness was measured, as well as sensitivity to SSC in service. All four of those pipes were microalloyed with columbium.

Identification of SSC-Sensitive Regions

In Pipes 1664 and EA2, the region of the HAZ that was sensitive to SSC was Subzone 2, which was heated intercritically during welding. This identification was made by examination of the surfaces of failed specimens after testing, and by examination of metallographic sections through the failure. Similar observations have been made by researchers at Nippon Kokan with specimens from production welds, as well as with specimens that were heat treated to simulate the various regions in the HAZ [4]. Table 3 summarizes the locations in which SSC initiation was observed for each pipe.

Examples of SSC cracks in Subzone 2 in a failed specimen from Pipe 1664 are shown in Fig. 4. That figure shows that several cracks were present, including the one that was

Pipe Identification	Location(s) of SSC Initiation	
 1664	Subzone 2	
EA2	Subzone 2	
DY1	Subzone 1	
Y52N	HAZ and base metal	
A-1	no SSC	
EA2, laboratory normalized	HAZ and base metal	

TABLE 3—Locations in which SSC initiation was observed.



FIG. 4—Sulfide-stress cracks observed in Subzone 2 in a specimen from Pipe 1664 tested in the NACE SSC environment: (a) fracture begins and (b) region circled in Part a.

responsible for failure. The main crack appears to have originated in Subzone 2 and then propagated through Subzones 1 and 3 during the final stages of fracture; similar observations were made in other specimens from both Pipes 1664 and EA2. Stepwise cracks also were observed, primarily in the base metal, but also in the HAZ. The SSC resembles the "Type I" SSC crack designated by Sumitomo researchers for SSC cracks that propagate through ferritic microstructures of relatively low hardness [6]. The higher magnification photomicrograph in Fig. 4 presents a closer view of the microstructure at the tip of one of the SSC cracks; the microstructure is similar to that shown in Fig. 2b for Subzone 2. No preferred crack path, such as along grain boundaries, was observed for any of the SSC cracks. Also, the cracks were not associated with any specific microstructural feature.

The SSC initiation in Subzone 1 in Pipe DY1, which was heated above the upper critical temperature during welding, is shown in Fig. 5. That identification initially was based on examinations of failed specimens, in a manner similar to that for the other pipes. Because the region that was sensitive to SSC was different for Pipe DY1 than for the other pipes studied, additional experiments were conducted in which the specimens were unloaded automatically when crack initiation was detected, to better identify the region of SSC initiation without the presence of extensive deformation. Those experiments also indicated that SSC initiated in Subzone 1 in Pipe DY1.

It is interesting to note the observation that was made with the specimens from a portion of Pipe EA2 that was normalized ($870^{\circ}C$ for 1/2 h, air cool) in the laboratory. The SSC in those specimens was not localized to Subzone 2, but was observed throughout the specimens, especially in the base metal. However, in the as-received condition, base-metal specimens from that pipe did not fail in SSC tests at a stress of 448 MPa (65 ksi), for test times of over 580 h. This observation indicated that normalizing had an adverse effect on the SSC sensitivity of the base metal, which had exhibited no SSC in the as-fabricated condition. It was supported



FIG. 5—Sulfide-stress cracks observed in Subzone 1 in a specimen from Pipe DY1 tested in the NACE SSC environment and automatically unloaded when crack initiation was detected: (a) fracture begins and (b) region circled in Part a.

by the observation of SSC in the base metal of Pipe Y52N, which was full-body normalized at the pipe mill.

Microstructural Characteristics of Sensitive Subzones

Subzone 2, which was found to be sensitive to SSC in Pipes 1664 and EA2, had a microstructure consisting primarily of polygonal ferrite with islands of M-A, in addition to bainite and pearlite. Subzone 1, which was found to be sensitive to SSC in Pipe DY1, also contained islands of M-A, but the M-A islands were much finer than those in Subzone 2, and the matrix microstructure was acicular ferrite. Because of this association, it was thought initially that the sensitivity to SSC in those subzones might be attributable to the presence of M-A islands. The laboratory-normalized base-metal specimens from Pipe EA2, which exhibited sensitivity to SSC, also exhibited M-A islands in the microstructure. Also, other researchers had made similar observations both in weldments and in simulated HAZ subzones [4], and tentatively identified M-A as the microstructural feature that was responsible for sensitivity to SSC. However, the low-temperature treatments and subsequent stress-relief heat treatments that were applied to transform and to soften those islands resulted in no effect on sensitivity to SSC. In addition, there were no direct observations of interactions between the SSC cracks and the M-A islands. Furthermore, the M-A islands were observed in both Subzones 1 and 2 in all of the pipes, and therefore could not account for Pipe DY1 exhibiting sensitivity to SSC in a different subzone than Pipes 1664 and EA2. Therefore, further microstructural characterizations by TEM were conducted to determine whether sensitivity to SSC could be attributed to unusual distributions of dislocations, precipitates, or other fine microstructural features.



FIG. 6—Sketch of sectioning sequence for samples for TEM: (a) initial sectioning and (b) sample removal by electro-discharge machining for subsequent electro-chemical for thinning.

TEM Examination

Thin foils for TEM studies were prepared from all three HAZ subzones in Pipes 1664, EA2, and DY1, and from the base metal of Pipes 1664, EA2, DY1, and Y52N. Samples approximately 0.75-mm thick were sectioned from each HAZ subzone, as is shown in Fig. 6, using electro-discharge machining (EDM). The samples were located approximately in the center of the subzone, near the inner surface of the pipe. Those samples were ground and polished by hand to a thickness of approximately 0.25 mm. Disks that were 3 mm in diameter then were punched from the 0.25-mm-thick samples, and were subsequently thinned electrochemically for TEM examination.

All of the thin foils that were examined contained relatively high dislocation densities and extensive tangles. No appreciable differences in dislocation structure were observed between foils from subzones that were sensitive to SSC and subzones that did not exhibit SSC. All TEM samples also contained very fine precipitates, which were observed on grain boundaries and within the grains, as well as on dislocations, but there were appreciable differences in the sizes of those precipitates among the subzones. Those differences in precipitate size appear to play an important role in sensitivity to SSC.

The precipitates in regions that did not exhibit sensitivity to SSC were of two size ranges, primarily 50 Å in diameter or finer, but with a small concentration of precipitates 500 Å in diameter or coarser; some of the coarser precipitates also were observed in subzones that were sensitive to SSC. Figure 7 presents TEM micrographs that provide examples of the precipitates in the base metal of Pipe EA2, which did not exhibit sensitivity to SSC in the as-fabricated condition. Figure 7*a* is a bright-field image showing the normal appearance of the precipitates in the TEM, and their relationship to the dislocations. Figure 7*b* is a dark-field image of the same field of view as in Fig. 7*a*, in which the diffracted electron beam is



FIG. 7—Transmission-electron micrographs from the base metal of Pipe EA2 showing extremely fine (<50 Å in diameter) precipitates and one coarse precipitate: (a) bright-field image and (b) dark-field image.

aligned such that all features (that is, the precipitates) with the same crystallographic structure and appropriate orientation appear bright. Often the precipitates are more readily visible in dark field than in bright field, and a more accurate measure of particle size can be made from the dark-field images.

Subzones that exhibited sensitivity to SSC in the laboratory experiments consistently contained intermediate-size precipitates that usually were not present in the other subzones or the base metal. In Subzone 2 of Pipes 1664 and EA2, and to a lesser extent in Subzone 1 of Pipe DY1, all of which exhibited sensitivity to SSC, most of the precipitates were approximately 100 to 200 Å in diameter. Figure 8 presents TEM micrographs that provide examples of the precipitates in Subzone 2 of Pipe EA2.

Table 4 summarizes the TEM observations of precipitates in the pipes that were studied. As shown in the table, all of the regions that exhibited sensitivity to SSC contained intermediate-size precipitates, although in Pipe DY1, Subzone 1, the density of those precipitates was appreciably lower than in the other SSC-sensitive subzones. The association of sensitivity to SSC with the presence of the intermediate-size precipitates was verified by the observation of similar intermediate-size precipitates in the base metal, both in the portion of Pipe EA2 that was normalized in the laboratory and in Pipe Y52N that was normalized at the pipe mill after welding. Those two materials exhibited sensitivity to SSC in the base metal. TEM micrographs in Fig. 9 show the typical appearance of those precipitates in the laboratorynormalized portion of Pipe EA2. Those precipitates were similar in appearance to the precipitates in the HAZ subzones in Pipes 1664, EA2, and DY1 that exhibited sensitivity to SSC.

The precipitates were identified by electron diffraction as being either columbium carbonitrides or vanadium carbonitrides. The two types of carbonitrides are essentially isomorphous, and cannot usually be distinguished by electron diffraction; even with the greater accuracy provided by X-ray diffraction, the two types of carbonitrides can be differentiated only with great difficulty. Energy-dispersive X-ray spectroscopy (EDS) of selected precipitates in the TEM indicated that the precipitates were rich in columbium, but contained no vanadium. An example of the superimposed X-ray spectra from a precipitate and from the adjacent matrix is presented in Fig. 10. Those spectra show high-intensity peaks for columbium (labeled Nb, for niobium) in the precipitate, which were absent in the matrix. The only peaks for the precipitate with a higher intensity than that for columbium were the iron and manganese peaks, which also were present for the matrix, and thus reflect the penetration of the electron beam into the matrix below the precipitate. Thus, the superimposed spectra indicate that the precipitate was rich in columbium. In addition, very low intensity peaks for vanadium are present in both spectra, indicating that there was no vanadium in the precipitate. Since EDS cannot detect carbon and nitrogen, it was not possible to determine more accurately the compositions of the columbium carbonitride precipitates.

Discussion and Conclusions

The detailed TEM examination of the subzones of the HAZs that were sensitive to SSC, as well as the base metal and those HAZ subzones that were not sensitive to SSC, indicated that sensitivity to SSC is associated with the presence of intermediate-size (100 to 200 Å) columbium carbonitride precipitates. Uniformly distributed intermediate-size precipitates were observed in all regions in which sensitivity of SSC was observed, and in none of the regions in which SSC did not occur. Pipe A-1, which was a Y52 pipe that did not contain columbium, and thus would not have columbium carbonitride precipitates in the HAZ, did not exhibit sensitivity to SSC.

Cracking by SSC was observed to progress essentially independently of any of the mi-





Location in Weld Region	Pipe 1664	Pipe EA2	Pipe EA2, Laboratory Normalized	Pipe DY1	Pipc Y52N, Mill Normalized
Subzone 1	many F," few C ^b	many F, few C		many F, some I ^c	
Subzone 2	many I	many I		many F	
Subzone 3	many F, few C	many F, few C		many F, few C	
Base metal	many F, few C	many F, few C	many I	many F, few C	many I

TABLE 4—Summary of TEM observations of precipitates in the four columbium-containing pipes.

^{*a*} F = extremely fine precipitates, 50-Å diameter and finer.

 h C = coarse precipitates, over 500-Å diameter.

^c I = intermediate-size precipitates, 100 to 200-Å diameter.

crostructural features that were observable by optical or scanning-electron microscopy. Thus, a microstructural feature that is responsible for sensitivity would not be associated solely with grain boundaries or any other readily visible features such as M-A islands. These observations, made among pipes with different compositions and strength levels, and in regions with differing thermal histories, provided support for the conclusion that sensitivity to SSC in the weld regions of microalloyed and controlled-rolled pipes is caused by the presence of columbium carbonitride precipitates in the approximate size range from 100 to 200 Å.

Comparison between Fig. 7 and Fig. 8 illustrates the difference in precipitate size between regions that were sensitive to SSC and regions that exhibited no sensitivity to SSC. Both of the regions in Figs. 7 and 8 were from the same pipe. Thus, that difference in precipitate size was a result of the thermal history in Subzone 2 during welding. The intermediate-size precipitates shown in Fig. 8 for Subzone 2 in Pipe EA2 apparently formed as the result of growth of the very fine precipitates that were present in the steel as fabricated, when that subzone was heated into the intercritical temperature range during welding. Those very fine precipitates (less than 50 Å) presumably were of the size range that provide grain refinement or strengthening or both, whereas the coarse precipitates (500 Å or greater) that were observed in many of the thin foils from various regions in the pipes probably formed during cooling through the austenite region prior to controlled rolling.

At least for Pipes 1664 and EA2, the heating-and-cooling cycle during welding in Subzone 1 either was too rapid to affect the precipitates, or was such that the precipitates were dissolved and reprecipitated. For Pipe DY1, the kinetics of precipitate growth apparently differed sufficiently from that in the other two pipes to cause the region of sensitivity to SSC to occur in Subzone 1, by the growth of many of the precipitates in that subzone; however, many fine precipitate growth in the base metal of Pipe EA2 also occurred during the laboratory-normalizing treatment, in which the metal was heated to a temperature slightly above the upper critical temperature but cooled relatively slowly. These observations reflect the complex interaction among temperature, composition, and cooling rate that governs precipitate growth [7] and, presumably, sensitivity to SSC in the weld region.

An investigation of SSC by Hoesch investigators [8] using full-size pipe sections identified differences in residual stresses as the source of sensitivity to SSC in the HAZ. In the present investigation, round-bar tension specimens were machined from the weld region, which relieved most of the residual stress in those specimens. Thus, residual stress should not be a significant factor in the present work. Residual-stress measurements made in each of the subzones using X-ray diffraction on electropolished metallographic sections were inconclusive [5].







FIG. 10-X-ray spectra for Pipe EA2, Subzone 2, matrix and precipitate.

Research by Mannesmann investigators [9] has suggested that sensitivity to SSC in line pipe is related to hardness variations in the weld region, but not conforming to the wellknown relationship between high hardness and sensitivity to this type of failure. Those investigators found that when the hardness in the HAZ was appreciably lower than that in the base metal and weld, SSC always occurred in the HAZ. It was inferred that the HAZ was stressed to a higher percentage of its yield strength than was the base metal or the weld metal, thus SSC initiated in the HAZ. The hardness data in Table 2 show a similar tendency for Pipes 1664 and EA2, for which the region of lowest hardness was HAZ Subzone 2, which was sensitive to SSC. However, Pipe DY1 exhibited slightly higher hardness in Subzone 1, which was sensitive to SSC, than in any other HAZ subzone or the base metal. Pipe Y52N failed in the base metal, which had the lowest hardness, as well as in Subzone 2, which had an intermediate hardness in the weld region. No SSC failures were observed in Pipe A-1. Tensile experiments using specimens that were instrumented with strain gages in the HAZ subzones also indicated that sensitivity to SSC was not related to local variations in yield strength, which was consistent with the hardness measurements [5].

The results of this investigation provide strong circumstantial evidence that SSC sensitivity in the HAZ of microalloyed pipe steels is the result of the growth of columbium carbonitride precipitates to approximately 100 Å in diameter during welding. Precipitate growth also has been observed under certain heat treatment conditions. The much finer precipitates that are normally present in the controlled-rolled condition probably do not affect a sufficiently large volume of the surrounding matrix to influence SSC, and the coarse precipitates appear to be too widely dispersed to have any observable effect. At present, the manner in which the intermediate-size precipitates contribute to sensitivity to SSC is not known. It is possible that the intermediate-size precipitates introduce strain fields in the surrounding matrix that could promote crack growth, or that they deplete the surrounding matrix of columbium or other elements and thereby form local galvanic cells in the aggressive environment. However, further research will be needed to establish the mechanism by which sensitivity to SSC develops with precipitate growth.

The observation of intermediate-size precipitates in different subzones of the HAZ for different pipes suggests that precipitate growth is influenced by many factors. Accordingly, it may be possible to control the growth of columbium carbonitride precipitates during welding or heat treatment, and therefore to control the sensitivity to SSC in the HAZ, by understanding the effects of composition, temperature, and cooling rate on precipitate growth. Further studies are under way to investigate the effects of steel composition and cooling rate from welding on the growth of columbium carbonitride precipitates.

Acknowledgments

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DISCUSSION

*R. N. Iyer*¹ (*written discussion*)—You stated that columbium carbonitride particles are responsible for SSC in the steel. Considering the roundedness of these particles (and hence low stress concentration), could you see evidence of cracks originating from these sites?

H. J. Cialone and D. N. Williams (authors' closure)—No evidence was observed of cracks originating from columbium carbonitride particles nor was cracking observed to originate from any other distinct microstructural features. The columbium carbonitride particles were quite small, so even in a scanning-electron microscope it was not possible to resolve them in metallographic sections through failed SSC specimens. Our statement that the intermediate-size particles are responsible for SSC was essentially based on circumstantial evidence, that is, whenever the particles were present, SSC occurred, and when they were not present SSC usually did not occur (although in some special circumstances, such as the presence of large inclusions, SSC occurred in the absence of particles). This consistent correlation between the presence of intermediate-size columbium carbonitride particles and SSC was unique among the microstructural features and metallurgical characteristics examined. Therefore, we conclude that these particles are responsible for sensitivity to SSC.

R. T. Pargeter² (written discussion)—Did you carry out TM-01-77 tension tests on parent material remote from a weld? It is common to find that parent pipe steels have a threshold of about 60% yield stress in this test.

H. J. Cialone and D. N. Williams (authors' closure)—The SSC experiments were conducted on parent material specimens for Pipe EA2. No failure was observed at an applied stress of 65 ksi in over 500 h. Thus, for Pipe EA2, the SSC threshold stress in the parent material appears to be well above 60% of the yield strength.

Factors Affecting the Susceptibility of Carbon-Manganese Steel Welds to Cracking in Sour Environments

REFERENCE: Pargeter, R. J., "Factors Affecting the Susceptibility of Carbon-Manganese Steel Welds to Cracking in Sour Environments," *Environmentally Assisted Cracking: Science and Engineering, ASTM STP 1049,* W. B. Lisagor, T. W. Crooker, and B. N. Leis, Eds., American Society for Testing and Materials, Philadelphia, 1990, pp. 169–239.

ABSTRACT: Weldments in structural and pipeline steels have been characterized in terms of hardness and microstructure (using light and electron microscopy) and resistance to stress corrosion cracking (SCC) in NACE TM-01-77 test solution. In addition, the propensities of the steels for pitting and hydrogen pickup in NACE solution have been determined, and stress corrosion fracture surfaces have been examined in the scanning electron microscope.

The principal factor affecting susceptibility to SCC was hardness, after which the presence of martensite was the only factor that clearly increased risk of cracking. While there were marked differences in hydrogen pickup and pitting tendency, no direct correlation with risk of cracking was observed.

It is concluded that the use of hardness limits is applicable to carbon-manganese steel weldments operating in sour environments, but that compositional ranges over which such limits are used need to be determined. Attention is also drawn to the fact that the inter/sub critical heat affected zone (HAZ) could be the most susceptible region for cracking in some steels.

KEY WORDS: fatigue (materials), environmental effects, carbon-manganese steels, welded joints, structural steels, pieplines, microalloyed steels, hardness, microstructure, electron microscopes, metallography, stress corrosion, cracking, pitting corrosion, fractography, martensite, hydrogen, heat affected zone

In order to cope with wet sour (that is, hydrogen sulfide (H_2S) containing) environments in oil and gas production and refining, a system of hardness control has been used for many years as, in general, softer structures are less sensitive to hydrogen-induced stress corrosion cracking (SCC). Upper limits of between 22 HRC [1] and 200 HB [2], equivalent to between about 245 and 210 VHN [3,4], have been imposed, and have been successful in ensuring a low incidence of sulfide SCC failures in practice.

Although upper hardness limits, such as 22 HRC, as specified by the National Association of Corrosion Engineers (NACE) [1], have become generally accepted for a wide range of steels in sour environments, it should be noted that hardness limits are only a convenient way of applying an observed relationship between strength and susceptibility to cracking. The NACE requirement is based on measurements using a large ball indenter in homogeneous material, and no consideration has been given to the effects of localized regions of high hardness such as are found at welded joints. Furthermore, it must be remembered that research work has demonstrated an effect of microstructure on susceptibility to cracking at

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	Material	Yield			Eler	nent, %	by wei	ght		
Cod	e Specification	N/mm ²	С	S	P	Si	Mn	Ni	Cr	Mo
 M1	BS 4360 50D	402	0.19	0.013	0.019	0.23	1.24	0.02	0.02	< 0.01
M2	API 5LX X65	509	0.10	0.007	0.015	0.42	1.48	0.04	0.03	0.01
M3	API 5LB	318	0.16	0.008	0.027	0.23	0.81	0.02	0.03	< 0.005
M5	API 5LX X65	485	0.03	0.004	0.013	0.20	1.18	0.19	0.02	0.008
M6	AP1 5LX X65	460	0.06	< 0.002	0.015	0.28	1.48	0.23	0.02	0.005
M7	BS 4360 43E	321	0.10	0.010	0.011	0.31	1.46	0.02	0.02	< 0.005
M8	BS 4360 50B	392	0.20	0.009	0.021	0.32	1.42	0.03	0.02	< 0.005

TABLE 1—Chemical composition and strengths of steels tested.

NOTES—Pb and Sn \leq 0.005, Co \leq 0.006 in all cases. All steels 25-mm thick flat plate.

constant strength or hardness [5-7]. In a review by Omar et al. [8], it was concluded that the sensitivity to SCC was a function of H₂S content, stress conditions, and microstructure, as well as hardness. Safe hardness limits depended on all of these factors.

The work reported in this paper has set out to investigate the material factors that affect cracking in welded joints in carbon-manganese (C-Mn) steels when exposed to sour environments.

Experimental Details

Parent Materials

The steels used are summarized in Table 1. The BS4360 50D structural steel (M1) was deliberately chosen to have a carbon equivalent at the upper end of the available range to ensure high hardenability and hence high heat affected zone (HAZ) sensitivity to hydrogen embrittlement. Three steels conforming to API 5LX Grade X65 were employed. Testing was concentrated on M2, a conventional low sulfur, calcium treated steel, whereas M5 and M6 were representative of the more recent generation of low carbon, very low sulfur, calcium treated steels with copper additions. Steel M5 also had a boron addition. Steels M7 and M8 were selected to provide specific HAZ microstructures at specific hardness levels.

Welding

Welding processes covering a range of arc energies of about 1 to 5 kJ/mm were employed for each steel. A manual metal arc bead on plate deposit was used to provide the lowest arc energy and most rapid thermal cycle. For the higher arc energies, full thickness butt welds were made. The welding processes and consumables were chosen to be representative of those used in practice on each steel type. Welding procedures and consumables are summarized in Table 2, with weld metal chemical compositions in Table 3. Photomacrographs of the welds are presented in Fig. 1.

Experimental Test Procedure

Stress Corrosion Tests—Rectangular bar specimens with their axes normal to the welding direction were machined as shown in Fig. 2. The weld reinforcement on the tensile face was left intact. Specimens were loaded in three-point bend over a span of 200 mm (Fig. 2). Load

		Elem	ent, %	by weigh	nt —		Contra		
v	Cu	Nb	Ti	Al	В	Ca	Equivalent	Pcm	Weld Numbers
0.003	0.01	0.034	0.006	0.015	< 0.0003	< 0.0003	0.40	0.26	W1,W2,W5
0.10	0.04	0.028	0.005	0.051	< 0.0003	0.0016	0.38	0.20	W3,W7,W11,W13
0.002	0.02	< 0.002	0.005	0.038	< 0.0003	< 0.0003	0.30	0.21	W4,W6,W10
< 0.002	0.29	0.041	0.020	0.043	0.0017	0.0021	0.26	0.12	W9,W15
0.050	0.36	0.044	0.003	0.033	< 0.0003	0.0025	0.36	0.17	W12
< 0.002	0.02	0.036	0.005	0.043	< 0.0003	< 0.0003	0.35	0.19	W14
< 0.002	0.02	0.047	0.004	0.027	< 0.0003	< 0.0003	0.44	0.28	W16

was applied using dead weights and a lever arm through knife edges, electrically insulated with Tufnel inserts. No allowance was made for stress concentrations due to the weld profile or for residual welding stresses in calculating the applied outer fiber stress. The test solution was prepared according to NACE Standard TM-01-77 [9] and consisted of 5% (NaCl) sodium chloride and 0.5% acetic acid in water, saturated with H₂S. The temperature was held at $25 \pm 3^{\circ}$ C.

Specimens were tested at different loads to define a crack/no crack threshold outer fiber stress for 720-h exposure. After completion of the test duration, all specimens were sectioned transverse to the weld to check for the presence and observe the location and morphology of any cracking. Hardness surveys were carried out on all sections using a Vickers machine under 2.5 kg load.

Pitting Trials—Samples approximately 25 mm square were cut from the parent materials and prepared as shown in Fig. 3. They were degreased with acetone and then exposed in the orientation shown to NACE solution for about 1300 h. An additional set of specimens was exposed with the original plate surfaces horizontal, the duration of exposure being 730 h. The tests with vertical surfaces were intended to give a comparison between original, dressed, and through-thickness cut surfaces, and the tests with the original surface horizontal reflected the orientation of the bend test specimens.

After exposure, the specimens were sectioned to reveal pitting morphology on the plate and cut surfaces, and one half of each of the 1300-h test specimens were cleaned in Ardrox 11 and examined under a binocular microscope. This gave qualitative information on the tenacity of the scale and the distribution of pitting.

Hydrogen Pickup Measurements—Rectangular samples of parent material about 10 by 10 by 20 mm, were prepared and divided into batches containing two samples from each parent material. Each batch was then placed in an individual container so that all specimens in that batch would be exposed to the same environment for the same time. The specimens were ground to a 320 grit finish on all surfaces and degreased with acetone.

Batches of specimens were exposed to the test environment for a range of times. Specimens were placed in liquid nitrogen immediately after removal from solution and stored at this temperature until it was possible to measure the diffusible hydrogen content. This was done by room temperature evolution over mercury using Y-tubes [10]. The specimens were cleaned prior to analysis by shot blasting.

							С	urrent, A	
Weld Number	Welding Process	Consumables	Position	Number of Passes	Preheat, °C	Interpass, °C	Max	Min	Avg
2,3,4, 9,12	Manual metal arc	BOC Ferex 7016, 4 mm	flat	1	100				180
1	Manual metal arc	BOC Ferex 7016, 4 mm	vertical up	10	ambient	35 to 75			120
5	Submerged-arc, single wire	Oerlikon SD3, 4 mm/Oerlikon OP 121TT	flat	8	ambient	<250	Side 1 400	Side 2 400	
6	Submerged-arc, tandem arc	BOC S1, 4 mm/ ESAB OK 1040	flat	2	ambient	<250	Side 1 750 800	Side 2 950 840	
7	Submerged-arc, triple arc	Oerlikon SD3, Mo, 4 mm/Lincoln 790	flat	2	ambient	<250	Side 1 1000 700 650	Side 2 1150 700 650	
10	Manual metal arc	Fleet weld 5 (AWS 6010) 3.25 and 5 mm	vertical down	22	75	60 to 100	215	100 (root)	152 (fill)
11	Manual metal arc	Thyssen Cel 80 (AWS 8010) 4 and 5 mm	vertical down	16	75	70 to 122	175	120 (root)	146
13	MIG	Thyssen K5Ni 0.9 mm Ar/CO ₂ (root) CO ₂ fill	vertical down	8	ambient	70 to 130	Root 185	Avg Fill 218	<i>Cap</i> 150
14	Manual metal arc	BOC Ferex 7016, 4 mm	flat	1	6				180
15	Manual metal arc	BOC Ferex 7016, 4 mm	flat	1	200			•••	180
16	Manual metal arc	BOC Ferex 7016, 4 mm	flat	1	160		•••		180

TABLE 2—Summary of welding procedures.

Weldment Examination

Optical Metallography—Weld metals and HAZs were examined in the optical microscope after polishing transverse sections to a 1 μ m diamond finish and etching in 2% nital. The microstructural constituents were counted using the International Institute of Welding (IIW) Subcommission IXJ [11] scheme and photomicrographs were prepared. Colony sizes were measured in the grain coarsened HAZ by counting intercepts along a line parallel to and between 0.025 and 0.1 mm away from the fusion boundary on a longitudinal section. Lath widths within colonies of ferrite with aligned second phase were estimated by counting intercepts across a number of colonies within the grain-coarsened HAZ. Weld metal reinforcement angles were measured on all sections through bead on plate welds, including those through tested specimens.

Scanning Electron Microscopy-Selected cracked plain bend specimens were cooled in liquid nitrogen and broken open for examination in the scanning electron microscope. Two

	Voltage, V		Ar	c Energy, kJ/r	nm		
Max	Min	Avg	Max	Min	Avg	Dimensions in m	ım
		25			1.0	bead-on-plate	
	•••	21	2.7	1.5	2.0	Runs 1 to 6	60° †
						Runs 7 to 10	10 J0
Side 1	Side 2					Runs 1.3.4.5	
35	32		3.0	2.5			, 25
				(root)			
						Run 2	60° _
Side 1	Side 2					Run 1	Y 1
30	30		4.9	4.1			4 23 105 \ ↓
40	40		(Side 2)	(Side 1)		Run 2	
6:1.1	sida 2					Run 2	
32	32						7 25
36	36		4.8	4.6			9
41	41		(Side 2)	(Side 1)			
25	24	25	2.1	0.8	1.3		60° 25
							<u></u> 2
34	25	25	2.7	0.8	1.7		60° 1 25
							<u>(*</u>
Root	Avg Fill	Cap					
23	23	22	1.04	0.43 (root)	0.94 (fill and cap)		3 2 2 2 2 2 2 2 3 2 2 5 3 2 5 3 2 5 3 2 5 3 2 5 3 2 5 3 2 5 3 2 5 3 2 5 3 2 5 3 5 3
		25			1.0	bead-on-plate	
		25			1.0	bead-on-plate	
		25			1.0	bead-on-plate	

cracks had not been open to the test environment and were examined without cleaning. The other specimens were cleaned in Ardox 11; this does not damage the fracture surface, but there will have been corrosion damage prior to cleaning.

Transmission Electron Microscopy—In order to investigate the microstructure of the HAZs in the low carbon boron treated steel, M5, thin foil specimens were extracted from the HAZs of Welds 9 and 15. In addition, a sample of parent material was heated to 1200°C and quenched in iced brine to produce martensite from which thin foils could be made for comparison with the HAZ structures.

Longitudinal sections taken from the HAZs were mechanically polished to a thickness of 1 mm, and then etched to identify regions of coarse grained HAZ. Disks, 3 mm thick, were removed and polished mechanically to 0.5 mm thickness before final thinning to perforation by electropolishing.

	_			Eler	nent, 9	% by w	veight		
Weld Number	Details	С	S	Р	Si	Mn	Ni	Cr	Mo
W1	Multipass MMA BOC Ferex 7016 PS 4360 SOD (M1)	0.17	0.013	0.016	0.22	1.21	0.01	0.01	<0.005
W 5	Multipass single submerged-arc SD3/OP 121 TT BS 4360 50D (M1)	0.15	0.011	0.018	0.25	1.27	0.01	0.02	< 0.005
W6	Two pass tandem submerged-arc S1/OK 1040 API 51 B (M3)	0.11	0.012	0.023	0.30	0.91	0.01	0.02	< 0.002
W7	Two pass triple submerged-arc SD3 Mo/Lincoln 790 API 5LX X65 (M2)	0.09	0.009	0.015	0.50	1.77	0.04	0.03	0.21
W 10	Multipass MMA Fleetweld 5 API 5L B (M3)	0.07	0.019	0.015	0.12	0.31	0.02	0.01	< 0.005
W11	Multipass MMA Thyssen Cel 80 API 5LX X65 (M2)	0.15	0.010	0.015	0.14	0.63	0.12	0.02	< 0.005
W13	Multipass MIG Thyssen K5Ni Ar/CO ₂ and CO ₂ API 5LX X65 (M2)	0.13	0.006	0.007	0.61	1.19	1.30	0.05	0.005

TABLE 3—Chemical compositions of weld metal.

Hardness Measurements—Detailed Vickers hardness surveys in weld metal and in grain coarsened HAZ were carried out at 2.5 and 30 kg load on a section through each weld, with surveys at 10 kg load according to the requirements of BS 4515 [12]. Microhardness measurements were made using a Leitz "Miniloader" machine on some specimens where there were sufficiently large colonies of martensite or ferrite carbide aggregate to encompass the impression.

Residual Stress Measurements—Residual surface stress measurements were made on selected bend test specimens using the center hole technique [13]. The weld bead reinforcement was removed with a shaper and final surface preparation was carried out using a hand-held grinder followed by removal of at least 0.25 mm with a hand-held rotary polisher. Gages were positioned on the fusion boundary in an orientation such that effects of stress gradients across the boundary were minimized [13].

Results

Optical Metallography and Hardness Testing-HAZs

Micrographs showing the grain coarsened HAZ from each weld are shown in Fig. 4, and the results of measurements of microstructure on the test welds are given in Table 4. The results of detailed HAZ hardness surveys at 2.5 and 30-kg load are included in Table 5 and of surveys according to BS 4515 [14] at 10-kg load in Table 6.

The HAZs containing significant amounts of martensite were produced in M1, M2, M7, and M8, when welded at low arc energy. Hardness levels of up to 516 microhardness with a 50-g load (HM50) and 463 2.5 VHN were recorded in W1, with slightly lower values of

			Elem	ent, % by we	eight			
v	Cu	Nb	Ti	Al	Со	As	CE	Pcm
0.002	0.01	< 0.025	< 0.002	<0.012	0.005	< 0.005	0.38	0.24
0.002	0.02	0.019	< 0.002	0.015	0.005	< 0.005	0.37	0.22
0.002	0.04	< 0.002	<0.002	0.016	0.005	< 0.005	0.27	0.17
0.06	0.07	0.017	0.008	0.033	0.01	0.006	0.45	0.22
0.002	0.05	< 0.002	0.005	<0.003	0.005	0.012	0.13	0.09
0.01	0.01	< 0.002	0.009	<0.003	< 0.005	<0.005	0.27	0.19
0.01	0.11	< 0.002	0.047	0.008	0.04	< 0.005	0.44	0.24

457 HM50 and 369 2.5 VHN in W2 in the same steel. At higher arc energy, martensite was replaced by ferrite with aligned second phase, and HAZ hardness was reduced to 254 2.5 VHN maximum. The martensite regions in W3 (M2) were too small for microhardness testing, and at 2.5-kg load, a maximum value of 322 VHN was measured. Higher arc energies on this steel eliminated martensite, and resulted in an increase in the proportion of polygonal and grain boundary ferrite. Low arc energy welds on M3, M5, and M6 produced little or no apparent martensite in the HAZ. For M3, the major constituents were ferrite with aligned second-phase and ferrite-carbide aggregate. For M5 and M6, the microstructure appeared to consist almost entirely of ferrite with aligned second phase. The carbon content of M5 was very low (0.03%), however, and hardness values of around 250 2.5 VHN suggested that some martensite could be present. In order to determine the appearance of martensite in such a low carbon steel in the light microscope, a sample was quenched from 1200°C into iced brine. The microstructure produced is shown in Fig. 5 and the maximum hardness was 287 2.5 VHN. The morphology of this quenched microstructure was sufficiently similar to parts of the HAZs of W9 and W15 to suggest that they did, in fact, contain some martensite, and this is supported by transmission electron microscope examination (see next section).

Transmission Electron Microscopy

Transmission electron micrographs from thin foils of M5 HAZs and quenched microstructure (see preceding section) are presented in Fig. 6a to c. All three micrographs show a closely similar microstructure consisting of heavily dislocated, closely spaced laths. The lath spacing (approximately 0.5 μ m) is considerably finer than that which can be observed on the optical micrographs, where a spacing of between 1.6 and 1.9 μ m was measured for W9



FIG. 1—Photomacrographs of welds.

and W15. Whereas the microstructure shown in Fig. 6c was present in all regions of the foils available for examination from the quenched microstructure, the regions shown in Figs. 6a and b, from W9 and W15, were found as localized regions in a much coarser grained, but still heavily dislocated, ferritic matrix, Fig. 6d. Owing to the very small area sampled by the thinned region of any foil, no estimate of the proportions of the two microstructures could be made for comparison between W9 and W15. Thus, both W9 and W15 contain some low carbon martensite, although it is not possible to say how much.



FIG. 1-Continued.

Optical Metallography and Hardness Testing-Weld Metals

In most cases, stress corrosion failures were in the HAZ, the exceptions being W1, W7, and W13. The microstructures of these weld metals are presented in Fig. 7. Optically, all three microstructures consist principally of acicular ferrite, with some polygonal ferrite along the prior austenite grain boundaries, and a small amount of ferrite with aligned second phase growing from this.

From Table 5, maximum hardness levels range between 177 and 296 2.5 VHN. There is little difference between the values measured with 2.5 kg load and 30 kg load, which is






FIG. 1-Continued.

presumably a reflection of the more homogeneous structure of the weld metals by comparison with HAZs.

Stress Corrosion Tests

The results of the stress corrosion tests are presented in Table 7, and threshold applied outer fiber stress has been plotted as a function of maximum hardness in Fig. 8. Error bars on stress show the highest no failure and lowest failure stress, and on hardness show the range of maximum values measured on individual test specimens.

A wide range of thresholds was determined, and there was a general trend of decreasing



FIG. 1-Continued.

threshold with increasing maximum hardness. There was, however, considerable scatter i this relationship. In the majority of cases, cracking initiated in the grain-coarsened HAZ In W7 and W13, however, cracking was only observed in weld metal, and for these it i weld metal hardness that has been plotted in Fig. 8. Some cracking was also observed i weld metal from W1, and it is of interest to note that the weld metal hardness was greate than the maximum HAZ hardness for both W7 and W13, close to it for W1, and at leas 202.5 VHN lower in all other cases. Cracking that had apparently initiated in the intercritica HAZ was observed in W9, but was usually found in conjunction with cracking in the grain



FIG. 1—Continued.

coarsened HAZ (Fig. 9). The stress corrosion crack induced in W5 at 120% parent material yield stress was also located in the intercritical HAZ (Fig. 10), but that at 130% initiated in grain-coarsened HAZ (Fig. 11). Stress corrosion cracking was always approximately normal to the plate surface (and the direction of stressing), but tended to follow the weld profile to a greater or lesser extent. Hydrogen pressure cracking was found in some sections from this weld.

Optical Metallography on Cracked Specimens

Photomicrographs showing HAZ cracking from selected specimens are presented in Fig. 12. Cracks were in general fairly wide, and had only limited branching. In all cases, cracking was clearly transgranular, both in the grain-coarsened HAZ and in the outer regions. Examples of weld metal cracking are shown in Fig. 13, and this is also entirely transgranular.

Scanning Electron Microscopy of Cracked Surfaces

Cracks from W2 and W4 were examined without any cleaning. The quasi-cleavage crack surface morphology was consistent with hydrogen cracking. A detail from W4 is presented in Fig. 14 along with an optical micrograph of the crack.

Cracks that had been exposed to the environment had to be cleaned. All surfaces had an appearance consistent with a hydrogen cracking mechanism. Examples from W1, W3, and W9 are shown in Figs. 15 through 17 together with optical micrographs of the cracks. A common feature of the crack surfaces was the presence of "flakes" standing in relief (for example, Fig. 16). The distribution and spacing is similar to that of carbides in the microstructure, and these are believed to be carbides. It is not known whether this etching is part







FIG. 1-Continued.

of the cracking mechanism or is a result of exposure to the sour environment after cracking, but similar effects have been observed in seawater [15].

Pitting Experiments

The results of the pitting experiments are summarized in Table 8, with comments on pitting of plain bend SCC specimens. Representative micrographs showing the range of severity and nature of pitting are presented in Figs. 18 through 23, and pitting observed on plain bend specimens is shown in Figs. 24 and 25.

Dressing the original surface appeared to have very little effect on the nature or severity of pitting. In some materials, however, there were significant differences between the surface in the vertical and horizontal positions. Steels M2 and M5 developed relatively severe sharp pitting in the horizontal position compared with minimal pitting in the vertical position for M2 and quite severe but rounded pitting for M5.² Examination of bend test specimens showed generally better correlation with the surfaces in the horizontal position, as might be expected.

It was observed that the scale was particularly adherent on M5 and M6, and particularly loose on M2. All these materials showed a propensity for sharp pitting and hence it appears that there is no simple correlation between the nature of the scale and pitting.

² Pitting has been termed "severe" when pits of 0.15 to 0.40 mm depth were observed on a metallographic section and "shallow" when no pits deeper than 0.10 mm were observed.



FIG. 1-Continued.



Hydrogen Pickup Measurements

Results of diffusible hydrogen analyses are presented in Table 9, and diffusible hydrogen pickup has been plotted as a function of time in Fig. 26. There are marked differences between the extent of hydrogen pickup in the different steels, maximum values ranging from 1.5 to 17.5 ml/100g. Some scatter in results of more than one day exposure was observed on M2 and M6, probably due to the blistering that was observed on the samples from these steels. For the three materials giving consistent results (with no blistering), an apparent peak in hydrogen content was observed. Such variations might be expected owing to changes in



FIG. 2-Bend test specimen configuration.



FIG. 3—Test specimen for pitting experiment. Specimen was immersed in NACE solution in the orientation shown.

corrosion rate as a scale builds up, or the effects of scale on hydrogen entry rate, and have been observed before. In work reported by Gooch [16], a fall in diffusible hydrogen content was observed between 100 and 525 h exposure in NACE solution for BS 4360 50D parent plate, 8018-C1 weld metal, and a 1.6% manganese weld metal. Initial peaks in hydrogen permeation rate through membranes in sour environments have been reported in the literature [15,17,18], but these peaks occur within about 10 h of immersion.

Residual Stress and Weld Bead Reinforcement Angle Measurements

The results of the surface residual stress measurements are presented in Table 10. The most significant result is the high value (average 216 Nmm⁻²) measured for W1, by comparison with the values averaging between 26 and 94 Nmm⁻² for the bead on plate welds. This would help to explain the high susceptibility to stress corrosion of W1, such that it cracked in NACE solution with no applied load. The differences between residual stresses measured on the bead on plate welds are not sufficient to account for the differences in their stress corrosion susceptibility, however. The differences in weld bead reinforcement angle for the bead on plate welds (Table 10) were also slight, ranging from 149 to 156°.

Discussion

In discussing the results of the present program of stress corrosion tests, it should be recognized that scanning electron microscope and optical metallographic data have confirmed that cracking has always been transgranular and quasi-cleavage rather than ductile, consistent with a hydrogen-assisted mechanism.

The factor most commonly reported as influencing the susceptibility of steels to hydrogenassisted stress corrosion is material strength level. Figure 27 shows data for smooth bend specimens taken from three separate references [19-21]. Despite different experimental techniques, there is close agreement between the three sets of data, showing a decrease in threshold stress with increasing strength. Similar good agreement between different sets of



FIG. 4—Microstructures of grain coarsened HAZs.



FIG. 4--Continued.



FIG. 4-Continued.



FIG. 4—Continued.



FIG. 4-Continued.



FIG. 4—Continued.



FIG. 4—Continued.



FIG. 4-Continued.

Wald				oport Cons	ions o tituen	of M its, %	ajor 6ª	Lath	Colony	Size, µm	Threshold Stress ^b % Parent Material	
No.	Plate	Details	F	CF	FC	М	AC	spacing, μm	Average	Maximum	Yield	
W1	M1	Multipass MMA, basic	0	8	25	24	43	1.51	15	60	0	
W 2	M1	Bead-on-plate	0	1	5	84	10		16	70	0	
W3	M2	Bead-on-plate	10	9	0	10	71	1.37	18	70	19 to 23	
W4	M3	Bead-on-plate	8	6	23	0	63	1.99	19	100	>140	
W 5	M 1	Multipass single submerged-arc	9	11	6	0	74	1.94	15	50	112 to 120	
W 6	M3	Two pass tandem submerged-arc	6	15	24	0	55	3.14	13	50	>120	
W 7	M2	Two pass triple submerged-arc	10	13	0	0	7 7	2.14	25	80	105 to 109 (WM)	
W9	M5	Bead-on-plate	9	3	0	0	88	1.69	16	80	20 to 26	
W 10	M3	Multipass MMA, cellulosic	12	9	24	0	55	1.78	13	50	>127	
W11	M2	Multipass MMA, cellulosic	15	13	6	0	66	1.67	15	40	109 to 118	
W12	M6	Bead-on-plate	1	7	3	0	89	1.45	9.8	70	56 to 64	
W13	M2	Multipass MIG	9	13	0	2	76	1.30	8.8	20	0 (WM)	
W14	M7	Bead-on-plate	0	5	0	36	59	1.19	11	40	32 to 40	
W15	M5	Bead-on-plate	6	5	Ó	0	89	1.86	16	60	>132	
W16	M8	Bead-on-plate	0	2	0	59	39	1.38	17	60	0 to 14	

TABLE 4—Summary of quantitative metallographic data for the grain coarsened HAZs.

^a F = polygonal ferrite, GF = grain boundary ferrite, FC = ferrite carbide aggregate, M = martensite, and AC = ferrite with aligned martensite, austenite or carbide. ^b Based on plain bend tests in NACE solution.

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Heat Affe Hardness, 2.5 VHN Details Hardness, 2.5 VHN Multipas MMA (basic) Maximum Minimum Average Bead-on-plate API 5L X66 (M2) 369 227 290 Bead-on-plate API 5L M(3) 46.3 32.2 412 Bead-on-plate API 5L M(3) 23.6 216 225 Muttipas single submerged-arc 24.0 179 197 API 5L M(3) 23.6 216 235 Muttipas single submerged-arc 24.0 179 197 API 5L M(3) 23.6 216 239 API 5L M(3) 25.4 209 239 API 5L M(3) 24.0 179 197 API 5L K56 (M2) 24.0 234 239 API 5L K56 (M2) 24.3 224 233	ffected Zone Han maximum						Advant		
Hardness, 2.5 VHN Details Hardness, 2.5 VHN Datalls Maximum Minimum Average 3460 SID (M1) 369 227 290 3450 SID (M1) 46.3 322 412 on-plate BS 4360 SID (M1) 46.3 322 412 on-plate API 5LX X65 (M2) 332 216 215 3450 SID (M1) 46.3 322 296 312 3450 SID (M1) 346.3 226 216 225 3450 SID (M1) 254 209 239 3450 SID (M1) 254 209 231 3450 SID (M1) 254 209 235 3460 SID (M1) 179 197 197 348 standem submerged-arc 240 179 197 348 striple submerged-arc 236 231 229 348 triple submerged-arc 236 231 239 348 triple submerged-arc 236 243 233 348 triple submerged-arc 243	Han Maximum					Weld	MICIAI		
Details Maximum Minimum Average qass MMA (basic) 369 227 290 4360 S0D (M1) 463 322 412 on-plate BS 4360 S0D (M1) 463 322 412 on-plate BS 4360 S0D (M1) 463 322 412 on-plate API SLB (M2) 236 216 225 on-plate API SLB (M2) 236 216 225 pass single submerged-arc 240 179 197 at SLB (M1) 236 210 239 pass tandke submerged-arc 240 179 197 pass triple submerged-arc 236 221 229 pass triple submerged-arc 236 221 229 pass triple submerged-arc 236 221 229 pass triple submerged-arc 236 231 224 pass triple submerged-arc 236 221 239 pass triple submerged-arc 236 231 239 pass triple submerged-arc 236 231	e Maximum	dness, 30 VF	Ţ	Haro	dness, 2.5 VF	Ŋ	Har	dness, 30 VH	z
pass MMA (basic) 369 227 290 4360 S0D (M1) 450 322 412 -on-piate RS 4360 S0D (M1) 453 322 412 on-piate RS 4360 S0D (M1) 453 322 312 on-piate API SLX X65 (M2) 236 216 225 on-piate API SLB (M3) 236 216 225 pass single submerged-arc 234 209 239 4360 S0D (M1) 236 210 179 197 pass single submerged-arc 240 179 197 pass tingle submerged-arc 236 221 229 f1 SLB (M3) 200-piate API SLX X65 (MS) 244 172 188 visit MA (cellulosic) 224 224 233 233 pass tingle submerged-arc 236 221 229 234 visit MA (cellulosic) 224 224 233 333 on-piate API SLX X65 (MS) 2277 172 188		Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average
Homplate BS 4360 5(D) (M1) 463 322 412 Homplate API 5LB (M2) 322 296 312 Homplate API 5LB (M2) 322 296 312 Homplate API 5LB (M2) 326 216 225 Homplate API 5LB (M3) 236 216 225 Has single submerged-arc 234 209 239 A360 50D (M1) 236 209 239 Pass tandem submerged-arc 240 179 197 Pass tandem submerged-arc 236 221 229 Pass triple submerged-arc 236 231 233 Pass triple submerged-arc 236	278	203	235	266	203	231	254	961	221
4-on-plate API SLX X65 (M2) 322 296 312 4-on-plate API SLB (M3) 236 216 225 4-on-plate API SLB (M3) 236 216 225 100 State Submerged-arc 254 209 239 238 State Submerged-arc 240 179 197 P1 SLB (M3) 236 216 229 P2 SLB (M3) 236 210 239 P3 SLB (M3) 240 179 197 P1 SLB (M3) 236 221 229 Pass tandem submerged-arc 236 221 229 Pass tandem submerged-arc 236 221 229 Pass tandem State API SLX X65 (M5) 243 224 233 Pon-plate API SLX X65 (M5) 227 172 188 Prise AAN Prise AAN 227 172 188	398	265	349	:	:	:	:	:	:
4-on-plate API 5LB (M3) 236 216 225 4-on-plate API 5LB (M3) 234 209 239 5 4360 50D (M1) 5340 50D (M1) 179 197 Pass tandem submerged-arc 240 179 197 P1 5LB (M3) 236 221 229 P1 5LB (M3) 236 221 229 P1 SLX X65 (M2) 243 224 233 Pass tipe submerged-arc 236 221 229 Pass TX X65 (M5) 243 224 233 Prist X X65 (M5) 227 172 188 Prist NAA Prist NAA 227 172 188	299	191	267		:	:	:	:	
tipass single submerged-arc 254 209 239 8 430 (M1) 240 179 197 Pass tandem submerged-arc 240 179 197 Pf 51B (M3) 236 221 229 pass triple submerged-arc 236 221 229 Per SL X66 (M2) 243 224 233 Per SL X65 (M5) 243 224 233 Per SL X65 (M5) 227 172 188 priss MAA (cellulosic) 227 172 188	226	206	218	:	:	:	:	:	;
PJ 3.1B (M3) PJ 3.1B (M3) pass tandem submerged-arc 240 179 197 pass tandem 236 221 229 py 51X X65 (M2) 243 224 233 d-on-plate API 51.X X65 (M5) 243 224 233 by 51 P, M3 (cellulosic) 2.27 172 188	236	188	209	218	163	197	213	172	197
Pass triple submerged-arc 236 221 229 Pf SLX X65 (M2) d-on-plate API SLX X65 (M5) 243 224 233 tripas MA (cellulosic) 227 172 188 bit SD A043	177	162	170	188	169	176	174	152	161
d-on-plate API 51.X X65 (M5) 243 224 233 inpass MM3 (cellulosic) 227 172 188 Di cti 2.M3.	237	221	226	274	240	247	266	327	242
tipass MMA (cellulosic) 227 172 188 DI st D (M3)	235	227	231	÷	:	:	:	:	:
	187	167	180	177	146	163	185	150	167
ttipass MMA (cellulosic) 270 196 264 PI 5LX X65 (M2)	249	210	233	206	191	187	204	165	188
d-on-plate API 5LX X65 (M6) 279 262 269	244	230	241		:	:	:	÷	•
tipass MIG API SLX X65 (M2) 279 243 266	266	240	255	296	258	275	295	220	270
d-on-plate BS 4360 43E (M7) 376 266 337	323	219	277	:	÷	:	:	:	÷
d-on-plate API 5LX X65 (M5) 254 230 241	227	216	222	:	:	:	:	•	÷
d-on-plate BS 4360 50B (M8) 363 342 353	333	243	288	:	;	:	:	÷	:

		Weld Number														
		W 1	W2	W3	W4	W 5	W6	W 7	W9	W10	W11	W12	W13	W14	W15	W16
							Сар									
Plate	1	158	160	197	161	164	152	206	171	161	200	191	206	170	185	166
HAZ	2	293	390	272	238	220	174	222	236	214	252	264	246	351	222	322
	3	265	357	272	228	206	175	225	251	182	245	262	250	362	232	319
Weld metal	4	205	238	238	217	201	164	240	222	152	185	227	293	252	189	236
	5	219	238	238	217	201	162	235	216	160	179	225	291	253	189	230
HAZ	6	279	339	270	227	206	173	222	238	208	242	270	282	350	209	325
	7	284	395	272	247	219	179	225	236	188	251	253	286	241	222	339
Plate	8	170	161	207	150	165	116	207	180	161	197	190	205	153	196	170
							Roo	Г								
Plate	9	161				167	151	210		151	192		163			
HAZ	10	309				232	181	228		172	240		216			
	11	302				228	182	221		177	230		242			
Weld metal	12	198				218	171	236		178	203		231			
	13	216				224	171	235		187	245		228			
HAZ	14	289				227	176	224		185	269		222			
	15	325				227	173	226		185	236		257			
Plate	16	161				169	141	203		157	198		180			
Maximum HAZ		325	395	272	247	220	182	228	251	214	269	270	286	362	232	339
Maximum weld metal		219	238	238	217	201	171	240	222	187	245	227	293	253	189	236

TABLE 6-Results of hardness surveys under 10-kg load according to BS 4515.

data [21–25] has been obtained for pre-cracked specimens, where a good relationship between defect tolerance parameter, $(K_{ISCC}/\text{yield stress})^2$, and hardness can be found, as shown in Fig. 28. In principle, therefore, the results of the stress corrosion tests in the present project should be considered initially in relation to strength. However, as welded joints are inhomogeneous, with quite marked changes in strength over very short distances, hardness was chosen as the best parameter for describing strength. This also follows current industrial practice of relating SCC sensitivity to hardness, even though there is not necessarily a fundamental relationship between them. Since crack initiation would be expected to be controlled by the most susceptible region, test results have generally been considered in terms of maximum hardness. A plot of threshold stress for 720 h exposure against hardness is presented in Fig. 8.

It is evident that there is considerable variation in susceptibility at a given hardness, and it is clear that there are other factors playing a part in determining material behavior. During this program, a number of measurements has been carried out in an attempt to explain some of the variability. The results of pitting experiments, hydrogen pickup measurements, weld bead reinforcement angle measurements, and residual stress measurements are reported in previous sections.

The pitting studies demonstrated that the steels tested show different pitting behavior in H_2S -containing environments. There was obviously a complex dependency of pitting on test conditions, and the nature and extent of pitting were not fully consistent between all tests. However, the main point to be made is that there is no correlation between the results of the pitting tests and the SCC behavior, so that effects of pitting, for example, in facilitating crack initiation, do not appear to be of major importance.

At the same time, some pitting observed after four to five weeks exposure to the NACE solution was quite severe. There were only three materials that showed any propensity for the formation of sharp severe pitting on the plate surface; namely, M2, M5, and M6. These were the three API 5LX X65 linepipe steels. They differ from the other four steels tested in that they contain calcium additions (0.0016 to 0.0025%), and were controlled rolled.





Further study is necessary to identify positively the reasons for the observed differences in pitting characteristics between steels.

While the hydrogen pickup measurements showed differences in the amount of hydrogen picked up by the various steels, there appears to be no direct correlation with the threshold stress for cracking. Steel M2 is slightly less susceptible to cracking (W3 and W11) than M3 (W4, W6, and W10) and M1 (W1, W2, and W5), while all three of these are considerably less susceptible than M5 (W9). After 14 days exposure, M1, M2, and M6 had picked up between 6 and 11 mL/100 g, whereas M5 has absorbed only 1 mL/100 g, with M3 being highest at about 14 mL/100 g.

In considering this apparent lack of correlation between hydrogen level and cracking, it should be remembered that the hydrogen determinations, which were carried out on unstressed parent steel, will not correspond exactly to the behavior of stressed, and inhomogeneous, weld samples. Indeed Smialowski [26] has reported greater hydrogen pickup by ferrite than martensite, and Phalen and Vaughan [27] have demonstrated that while this is the case in unstressed samples, stressed martensite picks up considerably more hydrogen than a similarly stressed ferrite-carbide structure. It is most probably the local hydrogen will diffuse along a stress gradient [27], and that factors such as work hardening exponent that affect the development of stress gradients will be relevant.

Despite the lack of correlation between parent material hydrogen pickup and cracking susceptibility, probably largely because of the differences between unstressed parent material and stressed transformed HAZs, similarly large spreads of hydrogen pickup values would be expected for the test specimens if it could be measured. This would undoubtedly affect the risk of cracking, and therefore contribute to scatter in the stress corrosion results.

There was little variation in weld bead reinforcement angle or surface residual stress between the bead on plate welds, and variations in the stress corrosion cracking: hardness relationship for those welds cannot be attributed to variation in these factors. Although both factors will vary to a greater extent between weld types and processes, neither is likely to have been a major contributory factor to overall scatter.

Considering the possible effects of microstructure on risk of cracking, published data suggests that three factors may be of importance, namely, the presence of martensite, the presence of coarse second-phase particles, and grain size. In work on a range of alloy steels in different heat treatment conditions, Snape [6] demonstrated that steels containing untempered martensite had the greatest susceptibility to SCC at strength levels below about 800 Nmm⁻², while quenched and tempered (Q&T) martensite showed the best resistance, being slightly better than normalized and tempered steels. These data are plotted in Fig. 29. The exceptions to these general trends were three Q&T steels that contained no untempered martensite, but did contain coarse carbides or sulfides, and had considerably greater susceptibility to cracking. The significance of martensite is also demonstrated by work on fabrication hydrogen cracking [28] where it has been found that the crack/no crack boundary remains at a fairly constant proportion of martensite and bainite, regardless of chemical composition.

In addition to Snape's observation that his three unexpectedly susceptible steels contained coarse carbides or sulfides, Fletcher and Smith [29] and Grobner et al. [30] both suggest an effect of carbide morphology on SCC resistance.

Gooch [31] reported that, whereas there was no effect of grain size on the SCC susceptibility of NCMV steel, an effect of the prior austenite grain size was apparent in HY80. He rationalized this difference in behavior in terms of the failure mode, the NCMV suffering



(a) Grain coarsened HAZ, W9.



(b) Grain coarsened HAZ, W15.

FIG. 6-Transmission electron micrographs from thin foils.

intergranular and the HY80 transgranular cracking. Several other authors have also reported an effect of grain size on hydrogen embrittlement or SCC [32-36], and the observed effect appears to depend on strength, transformation products, and whether attack is intergranular. An effect of ferrite grain size on weld metal fabrication hydrogen cracking has been reported by Hart [37]. He found that at low hydrogen levels and at the same hardness, ferrite with aligned second phase had a lower resistance to cracking than much finer grained acicular ferrite structures. Similarly, Pussegoda and Tyson [38] compared a quenched high-strength low-alloy (HSLA) steel and a grain coarsened HAZ in this steel of similar hardness, and found that the coarser HAZ structure was more susceptible to hydrogen embrittlement.



(c) Parent material (M5) after heating to 1200°C and quenching into iced brine.



(d) The appearance of the matrix in W9.

FIG. 6-Continued.

In the present work, measurements of grain or colony size have failed to provide a consistent explanation for the variation in susceptibility to stress corrosion. These measurements are presented in Table 4, along with the threshold stresses derived from plain bend tests in NACE solution. Average colony sizes ranged from 11 to 18 μ m for welds with thresholds of less than 40% parent material yield stress in the plain bend tests in NACE solution, and from 13 to 19 μ m for welds with thresholds of greater than 100%. There was an apparent correlation between lath spacing and susceptibility, but it is likely that this is just a reflection of the lower hardness associated with such coarser microstructures. Thus, although in principle it might be expected that finer (and presumably tougher) weld area microstructures would have increased resistance to stress corrosion, it is not possible, from



FIG. 7—Weld metal microstructures.



FIG. 7—Continued.

						Hardness	2.5 VHN				
Weld		Plate		Applied Fiber	l Outer Stress	HAZ	Weld	Time Flapsed		Thre str	shold ess
Number	Code	Specification	Weld Type	N/mm ²	%, σ _y "	Maximum	Maximum	h	Result ^h	N/mm ²	$\%$. σ_y^a
w4	М3	API 5LB	bead-on-plate	444	140	251		743	NF		
			-	413	130	224		768	NF	>444	>140
				409	129	243		748	NF		
				408	128	258		747	NF		
				408	128	227		744	С		
				381	119	270		724	NF		
				381	119	254		747	NF		
				365	114	270		698	NF	408	128
				318	100	258		712	NF		
W10	M3	API 5LB	multipass, MMA,	340	107	201	177	710	NF	>403	>127
			cellulosic	403	127	205		743	NF		
W6	M3	API 5LB	two pass, tandem	318	100	198	177	712	NF	>382	>120
			submerged-arc	382	120	240		672	NF		
W2	M1	BS 4360 50D	bead-on-plate	397	99	454		744	С		
			•	355	83	428		721	С		
				312	78	350		721	С		
				311	78	420		723	С		
				288	72	463		771	NF	0	0
				221	55	437		768	С		
				0	0	387		727	С		
				0	0	420		748	C		
W1	M1	BS 4360 50D	multipass, MMA	432	109	258	266	41	F		
			• '	215	54	270		718	С		
				130	33	272		718	С	0	0
				59	15	306		745	С		
				0	Ó	266		744	С		
W5	M1	BS 4360 50D	multipass	526	130	244		816	Ē		
	_		submerged-arc	483	120	270		720	C		
			-8	450	112	230		832	NF	483	120
				397	99	218	218	830	NF		

TABLE 7-Results of plain bend tests in NACE solution.

						Hardness	2.5 VHN				
Wold		Plate		Applie Fiber	d Outer Stress	114.7	Weld	Time		Three	shold ess
Number	Code	Specification	Weld Type	N/mm ²	$\%, \sigma_y^a$	HAZ Maximum	Maximum	h h	Result ^b	N/mm ²	$\%, \sigma_y^a$
W3	M2	API 5LX X65	bead-on-plate	554	109	327		718	C		
				338	66	311		697	С		
				186	37	333		768	С		
				143	28	292		721	С	119	23
				119	23	296		721	С		
				99	19	292		698	NF		
				95	19	322		793	NF		
W13	M2	API 5LX X65	multipass MIG	555	109	302	296	750	C (WM)		
				273	54	327		768	C (WM)		
				110	22	287		746	C (WM)		
				0	0	287		746	C (WM)		
WIL	M 2	API SLX X65	multipass, MMA,	669	131	266	206	710	C		
			cellulosic	602	118	285		792	NF	599	118
				599	118	251		146	F		
		. D		555	109	254		750	NF		
W /	M2	API SLX X65	two pass, triple	557	110	262	274	168	F (WM)		
			submerged-arc	555	109	247		672	C (WM)		
				535	105	266		816	NF	555	109
				486	95	236		723	NF		
		_		419	82	229		744	NF		
WQ	M5	API SLX X65	head-on-plate	468	96	251		745	<u> </u>		
	141.5	ALL DEA A05	ocad-on-plate	204	61	231		745	č		
				161	33	247	• • •	725	Č	127	30
				127	26	251		702	Č	127	50
				06	20	255		1178			
				64	13	2.34		726	nitted		
				04	0	240		726	pitted		
W15	M5	API SLX X65	head-on-plate	630	132	233		743	pitted		
	141.0	1111 3.274 7105	ocad-on-plate	484	100	233		742	NE	>630	>132
				387	70	237		768	NE	2 000	- 152
				382	79	221		747	NE		
				275	57	230		725	NE		
W12	M6	API 51 X X65	head-on-plate	450	114	230		832	E		
	1010	1111 3071 7103	ocud on plate	204	74	206		786	Ċ	266	64
				266	64	290		821	Č	200	04
				236	56	200		707	nitted		
				147	37	294		726	pitted		
				14/	0	292		726	pitted		
W16	M8	BS 4360 50B	bead-on-plate	392	100	383		720	С		
			•	274	70	350		720	С		
				235	60	357		720	pitted	54	14
				196	50	350		720	С С		
				103	26	351		768	С		
				54	14	376		768	С		
				0	0	360		746	NF		
W/14	N47	DC 4260 42F	hand on -late	221	100	2/7	·	720			
W 14	IVI /	DS 4300 43E	beau-on-plate	321	100	307		720			
				193	00	351		720	NF		
				137	49	330		/4/		120	40
				133	42	344		909 700	NF	128	40
				128	40	3/3		720			
				105	32	334		1120	INP NTC		
				0	U	303		1120	INF _		

TABLE 7—Continued

^{*a*} σ_y = parent material yield stress. ^{*b*} F = fracture, C = cracking, NF = no failure, and WM = weld metal.









the present work, to ascribe variations in the relationships between hardness and threshold, directly to the morphology of the transformed structure.

The point counting results in Table 4 do, however, indicate a dependence of cracking susceptibility on the presence of martensite, which would be consistent with Snape's results just discussed. All the microstructures that clearly contained martensite from optical examination have been found to have relatively low thresholds (see Table 4) apparently regardless of the surrounding microstructure. The only remaining welds with threshold applied stress below the parent material yield stress are Welds 9, 12, and 13.

No martensite was initially identified optically in the HAZ of W9 (bead on plate, lowcarbon boron-treated steel) although comparison with a quenched microstructure from this parent material suggested that the HAZ did in fact contain some martensite. Subsequent transmission electron microscopy confirmed the presence of regions of martensite (see section on Transmission Electron Microscopy). Similarly, although no martensite was identified optically in the HAZ of Weld 12, it is likely that the 3% ferrite carbide aggregate counted was, in fact, martensite, and certainly this is consistent with the maximum hardness of approaching 300 2.5 VHN at a carbon content of 0.06%. An optical micrograph of this HAZ is shown in Fig. 4k. Finally, Weld 13 cracked in the weld metal with no applied load. In this case, martensitic microphases would be expected within the weld metal microstructure. It may therefore be postulated that some martensite is necessary in the microstructure of a C-Mn steel welded joint for a SCC threshold of less than parent material yield stress in NACE solution.

Thus, to summarize the factors affecting the susceptibility of different welded joints to SCC in a given environment, the clearest correlation has been found with hardness. Consideration of other factors, namely, parent material hydrogen pickup, parent material pitting behavior, weld bead profile, residual stress, and microstructure, has indicated that although most of these items have probably contributed to the variations in the results, the most important feature after allowing for strength is microstructure, and in particular the presence or absence of martensite.

Application of Results

Hydrogen-assisted SCC is currently guarded against by stipulating hardness limits with no regard for microstructure or other parameters. There are clearly limitations to this approach as well demonstrated by the range of cracking thresholds at a given hardness level generated in this program. However, if the principal microstructural factor is the presence or absence of martensite, this would be expected to act in the same sense as the effect of hardness per se. In most materials, the presence of martensite would result in higher maximum hardness, in conjunction with greater susceptibility to cracking. Hardness alone will not, however, indicate the presence or absence of martensite, nor whether any "critical" amount is present. This is specifically the case for very low carbon steels. As discussed previously, it is probable that the low threshold for Weld 9 is associated with the presence of martensite in the HAZ, despite a maximum hardness of only 251 2.5 VHN, the carbon level being 0.03%. Thus, it may, in the future, be necessary to stipulate compositional ranges over which hardness limits are applicable. With sufficient experimental data, it might indeed be possible to generate a cracking risk index that would account for both hardness and compositional factors. It is considered that such an experimental approach is necessary since it is not currently possible to quantify the proportion of martensite and the hardness of that martensite from a given steel composition and weld thermal cycle. From these two, it would



(c) Outer regions of HAZ shown in (b).

FIG. 12-Micrographs of cracking in HAZ.



(d) Grain coarsened HAZ of low carbon, boron treated steel.

FIG. 12-Continued.



FIG. 12-Continued.

in principle be possible to predict a critical resultant bulk hardness for SCC. Without further hardenability data, however, it can only be remarked that lower carbon steels will contain more martensite at a given hardness level, and will therefore be expected to be more sensitive to SCC at that hardness.

During this program, some test specimens from each of two weldments were observed to crack preferentially in the inter/sub critical HAZ. This type of behavior has been observed by other workers [39-41] and also in service failures [42], and has been attributed to one or a combination of three factors. Firstly, this region of the HAZ is typically softened both with respect to other parts of the HAZ and the parent material particularly in controlled rolled steels. In a ductile material, hydrogen may lower both the yield and the ductility [43], and therefore a soft microstructure may be sensitive to crack initiation. In addition, there will be a strain concentration in this soft region under high transverse stresses. Second, the rapid thermal cycle can result in the formation of retained island martensite in the intercritical HAZ. Third, cracking has been found to initiate at regions of retained pearlite within the intercritical region [39]. In materials susceptible to hydrogen pressure cracking, the linking of pressure cracks under the influence of in-plane stressing may also occur. However, in the present program, it has been found that in welds where the maximum HAZ hardness was below ~ 250 VHN, no cracking could be induced in plain bend tests in NACE solution at applied stress levels of up to parent material yield. Regions of high hardness therefore appear to pose the highest risk from SCC, and the use of maximum hardness limits is to some extent justified. Nevertheless, in materials other than those tested in this program, the possibility of high inter/subcritical HAZ susceptibility to SCC could be envisaged.



FIG. 13—Micrographs of cracking in weld metal.


(a) SEM of fracture surface of crack remote from the environment.

FIG. 14—Cracking in W4, test BD (NACE solution, 408 N/mm² (128% parent material yield) outer fiber stress, 744 h test duration).

Possible examples are steels with alloying that could promote the formation of island martensite in the intercritical HAZ, and quenched and tempered steels that would soften significantly in inter/sub critical regions. Thus, further limitations on the steels for which hardness limits are applicable may be necessary.

Conclusions

A program of stress corrosion testing in an acid, sour (H_2S containing) environment (NACE solution) has been carried out on C-Mn steel welded joints. From these test results and associated measurements and metallographic data, the following conclusions have been drawn.

- 1. Susceptibility to cracking increases with increasing hardness.
- 2. In addition to the effect of hardness per se, there was an effect of martensite, in that all welds exhibiting a low cracking threshold contained some martensite.
- 3. There was no clear correlation between microstructural type or dimensions and susceptibility to cracking, other than the effect of martensite.





(a) SEM of fracture surface of crack after cleaning.

FIG. 15—Cracking in W1, test BF (NACE solution, no applied load, 744 h test duration).

- 4. Pitting was observed in NACE solution, and differences in the nature of pits on different parent materials were observed. There was no correlation, however, between the nature of pitting and the susceptibility to cracking.
- 5. Marked differences in hydrogen pickup were measured in samples of parent material exposed to NACE solution. These differences in pickup between different materials did not correspond to the susceptibility of welds in those materials to cracking.
- 6. The currently accepted use of hardness limits is supported for welds in C-Mn steels in so far as the risk of cracking increases with increasing weld area hardness.

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	M1	M2	M3	M5	M6	M7	M8
			1300 н				
Original surface, vertical	r	nil	R	R	r	R	r
Dressed surface, vertical	r	nil	R	R	r	R	r
Through-thickness cut	R	r	R	S	R	r	S
Distribution of pitting	extensive	extensive	sporadic	extensive	occasional	extensive	extensive
Adherence of scale	average	loose	average	tight	tight	average	average
			730 н				
Original surface, horizontal	r	S	R	S	nil	R	nil
		~720 н (р	LAIN BEND	tests)			
Original surface, horizontal	r	r ^a	R	S	S	r	r

TABLE 8—Results of pitting experiments.

NOTES—S = sharp

S = sharpR = rounded upper case = severe (0.15 to 0.40 mm), lower case = shallow (<0.10 mm).

^a Occasional sharp intrusions at bottom of rounded pits.



(a) SEM of fracture surface of crack after cleaning.

FIG. 16—Cracking in W3, test BN (NACE solution, 119 N/mm² (23% parent material yield) outer fiber stress, 721 h test duration).



	Diffusible Hydrogen Collected, mL/100 g					
	M1	M2	M3	M5	M 6	
		NACE SOL	LUTION			
1 day	6.28	6.82	3.99	1.13	2.67	
•	6.46	6.93	3.01	1.12	2.93	
2 days	9.06	9.77	6.87	1.34	1.72	
	8.50	4.93	6.87	1.43	5.68	
4 days	10.99	6.83	16.61	1.10	7.99	
2	10.93	9.78	17.50	1.23	5.40	
14 days	10.86	6.42	13.54	1.05	8.93	
,	6.16	11.36	14.79	1.13	5.63	
30 days	10.51	6.38	4.68	0.86	1.88	
<i>y</i> -	9.28	8.31	4.68	0.85	1.12	

TABLE 9—Results of hydrogen pickup measurements.



(a) SEM of fracture surface of crack after cleaning.

FIG. 17—Cracking in W9, test BC (NACE solution, 468 N/mm^2 (96% parent material yield) outer fiber stress, 745 h test duration).





		Measured Residual Stress, Normal to Fusion	Bead Reinforcement Angle,°		
Weld Number	Details	Surface, N/mm ²	Maximum	Minimum	Average
	Bead-on-plate, API 5LB (M3)	33, 20 averaging 27	153	144	150
W1	Multipass MMA, BS 4360 50D (M1)	151, 280 averaging 216			
W2	Bead-on-plate, BS 4360 50D (M1)	30, 22 averaging 26	164	141	149
W3	Bead-on-plate, API 5LX X65 (M2)	101, 86 avcraging 94	170	144	155
W9	Bead-on-plate, API 5LX X65 (M5)	56, 28 averaging 42	160	149	156
W12	Bead-on-plate, API 5LX X65 (M6)	58, 57 averaging 58	153	151	152

TABLE 10-Results of residual stress and weld bead reinforcement angle measurements.



FIG. 18—Shallow rounded pitting on the as-received surface of M8.



FIG. 19—Severe rounded pitting on the as-received surface of M5.



FIG. 20-Severe sharp pitting on the surface of M2 in the horizontal position.

OU3858

80u



FIG. 21—Shallow rounded pitting on cut surface of M2.



FIG. 22—Severe rounded pitting on cut surface of M3.



FIG. 23—Severe sharp pitting on cut surface of M8.







FIG. 24(b)—Detail of pitting remote from the weld.



FIG. 24(c)—Detail of pitting close to the weld.













FIG. 27—Relationship between strength and threshold stress for cracking in saturated H_2S environments taken from the literature.



FIG. 28—Data from K_{ISCC} testing carried out in NACE solution reported in the literature.



FIG. 29—Data from Ref 6 showing the effects of microstructure on sulfide stress corrosion cracking.

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Modeling and Analysis

A Mechanics-Based Analysis of Stress-Corrosion Cracking of Line-Pipe Steel in a Carbonate-Bicarbonate Environment

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ABSTRACT: A model for stress-corrosion cracking (SCC) crack initiation and early growth has been developed and used to rationalize the SCC susceptibility observed in tapered-tension tests of line-pipe steels that have been tested at a high maximum stress, with a small amplitude load-controlled cyclic component in a carbonate-bicarbonate environment. Results presented here indicated a good correlation between the observed susceptibility and that predicted with the model. The main conclusion is that SCC models can be used to rationalize experimentally observed cracking behavior and as such can be used to identify conditions for cracking or mitigation beyond the scope of the test conditions, including line pipe applications.

KEY WORDS: stress corrosion cracking (SCC), initiation, propagation, free surfaces, models, prediction, slow-strain-rate test, tapered-tension test, line pipe steels, dissolution, creep, plasticity, fatigue (materials), cracking, environmental effects

Stress-corrosion cracking (SCC) occurs occasionally in line-pipe steels. Reviews of this cracking indicate that the environment is carbonate-bicarbonate and that the cracking is primarily intergranular [1]. Over the years metallurgical and electrochemical parameters have been identified as playing a role in the process [2]. The significance of strain rate and its relationship to the service loading also has been argued in that dissolution is indicated as the controlling mechanism [3]. While much has been learned about the mechanism of cracking, very little has been learned about how to directly relate the nucleation and growth of cracks to the loading, the metallurgy, and the environmental parameters.

The continual development of new line-pipe steels, the possible development of reliable in-line inspection (ILI) tools to detect SCC, and the occasional discovery of cracking colonies during field surveys have recently centered attention on methods to rank line-pipe resistance to SCC and characterize crack-growth rates. Ranking line-pipe resistance to SCC may be done in terms of a threshold stress for nucleation of SCC or the rate of crack growth at some crack depth beyond nucleation. Estimating remaining life of cracks located by an ILI tool or confirmed in a field survey involves only crack growth rate data or data that define a threshold stress for continued growth. Recent attention, therefore, has focused on experimental protocols to assess susceptibility, determine thresholds, and establish growth rate behavior. The tapered-tension test (TTT) [4] has been developed to determine stress thresholds for crack nucleation, whereas several different prenotched or precracked geometries have been or are now being used to assess crack growth. Attention has also focused on

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modeling SCC thresholds and crack growth behavior so that data developed under laboratory conditions can be adapted to assess field cracking situations. This paper presents the development and validation for a model that is being developed to deal with the threshold for and the growth of SCC cracks in line pipe up to about 500 μ m deep.

Considerations in Modeling SCC in Line Pipe

Background

This paper embraces factors that control cracking related to the pipe material and service loading. Thus, the development of the electrochemical conditions for cracking involving breakdown of the coating, the development of the environment, and so on, are presumed to have already occurred. The view taken is that if one cannot relate the SCC behavior of different specimen geometries made of the same steel, subjected to different load histories, and tested under known controlled electrochemical conditions in the laboratory, then it will be nearly impossible to relate the results of any laboratory test to field conditions. This paper represents the first step in this process in which the SCC behavior for one laboratory test geometry and loading provides the independent basis to predict the SCC behavior of another geometry under another set of loading conditions. It is assumed in light of past work that dissolution is the controlling mechanism. It is asserted that dissolution controlled crack growth observed in a test represents the total time in the test during which dissolution can occur multiplied by a constant rate of dissolution (the Faradaic rate). The cracking velocity, therefore, is always less than or equal to the rate of dissolution. The keys to implementing this assertion are (1) to identify the conditions that "turn-on" or "shut-off" dissolution, and (2) to calculate the accumulated time that satisfies these conditions. Under this assertion the maximum cracking velocity is the theoretical maximum rate of dissolution (from Faraday's law of electrolysis). The minimum SCC velocity is zero such as could occur if strain rates were so slow as to permit repassivation without dissolution or if the mechanical response precluded inelastic flow.

Because the model focusses on susceptibility to SCC, test protocols developed to judge susceptibility have been used. The protocol used to "characterize" the material and serve as the reference for predictions is the slow strain rate test (SSRT) [5]. This test involves the continuous straining of an axial specimen at constant strain (displacement) rate, with susceptibility evident in cracking frequency and depth, as well as in other parameters like reduction in area. The TTT [6], developed to be more discriminating of SCC susceptibility once the cracking environment was established, is the test case being predicted using the SSRT data. The TTT test involves the small amplitude cyclic axial loading of a bar whose cross-section varies to produce a different stress as a function of position. The test is conducted at a very high mean stress, with susceptibility evident in crack frequency and depth at locations along the bar above a threshold stress for cracking. Thus, the characterizing test is done in strain (displacement) control under a monotonically increasing control condition while the result being predicted represents load control at a high mean stress with a superimposed small amplitude stress cycle.

Modeling Dissolution-Based SCC at Free Surfaces

There have been many attempts to model environmentally assisted cracking (EAC) behavior using elements of electrochemistry, metallurgy, and mechanics [6-9]. Parkins [10] suggests that EAC represents a spectrum ranging from complete stress-dominated behavior to corrosion-event dominated behavior (corrosive attack). Accordingly, EAC models should provide for the range of stress/environment interaction behavior rather than for the stress controlled or corrosion controlled extremes.

Recently, models for SCC that are consistent with the spectrum suggested by Parkins for material-environment systems that could be rationalized as dissolution controlled have been developed, first for macrocrack growth [11,12] and thereafter for crack nucleation and microcrack growth [13]. Because dissolution occurs at clean surfaces and at a high rate until a film forms (repassivation), continued dissolution at that rate would require the evolution of clean (freshly exposed) surface. Clean surface develops with inelastic strain at levels large enough to cause film rupture, thereby exposing new steel. Such inelastic strain occurring in individual grains results in shape changes and exposes new surfaces via slip within the crystalline matrix. Because of compatibility requirements, shape changes in the grains cause inelastic deformation at grain boundaries, which also exposes new surfaces at these interfaces. As such, inelastic deformation associated with slip could be related to both transgranular and intergranular SCC origins and crack paths.²

The cracking behavior of laboratory specimens subjected to cyclic loading was modeled in Refs 11-13 using data developed from another very different geometry and loading. It was postulated that if metallurgical, environmental, and mechanical similitude were achieved between the specimens, the behavior of one specimen geometry and loading could be predicted from reference data developed using another specimen geometry and loading. Metallurgical similitude was provided for by using samples cut close to one another from the same plate of steel. Environmental similitude was achieved by ensuring accessibility of the environment with otherwise identical electrochemical conditions. Mechanical similitude was achieved by matching the stress-strain conditions that result in cracking for the reference specimen geometry in the other geometry for its loading history. Given that dissolution occurs at a nearly constant rate if conditions for continued (bare-surface) dissolution are met, predicting the cracking behavior in one specimen from that of a second requires (1) identifying when the conditions for dissolution are satisfied and (2) finding a test that maximizes the time that satisfies these conditions, which can serve as a reference test specimen geometry and loading.

Conditions for cracking to occur used in Refs 11-13 relate to exceeding a critical strain and to the interval of strain rate that causes dissolution. The critical strain that creates fresh surface for dissolution, either within the grain or at the grain boundary, is assumed to be the proportional limit strain occurring at the onset of plasticity.³ The strain rate must be fast enough to prevent intervening repassivation, yet slow enough that failure due to plastic flow does not outpace dissolution. These upper and lower bounds on strain rate lead to a range or "window" in strain rates that produces cracking, whereas rates outside the window do not lead to continued cracking dominated by SCC.⁴ Test conditions that lie within this range or window in rates "turn-on" SCC—otherwise, dissolution is "shut-off." Satisfying these conditions for cracking between two specimens satisfies the mechanics requirement for similitude between the situations being compared. The condition to satisfy strain rate

 2 The premise that dissolution requires inelastic action to expose new surface is not new. For example, slip-dissolution concepts (for example, see Ref 14) involve this same premise. However, the present use of this premise is not slip-step based and focused on transgranular cracking. Rather, it is presumed that inelastic action within grains causes incompatible displacements along grain boundaries so that intergranular cracking may be addressed.

³ More generally it could be stated as the strain for film rupture, which in the present case was determined empirically to be the proportional limit (a 0.0001 strain offset was used, but because of the stress-strain response of the steel examined similar results would be obtained over a range of off-sets).

⁴ Rates at the lower end would cause dissolution at grain boundaries and other features that develop inelastic action, effectively etching these regions. However, the depth of attack would be minimal, limited by the time until repassivation. Rates at the higher end would likewise limit the contribution of dissolution, not because of repassivation but because other mechanisms such as creep or fatigue cause crack advance at rates that are much larger than dissolution. Cracking still occurs and there may be a component of SSC (see Parkin's spectrum [10]). In this limit, other mechanisms control or dominate cracking.

or a window of strain rates has been utilized for some time in analysis of SCC (for example, Refs 10 and 15), whereas the condition to achieve a minimum strain has not been sufficiently emphasized nor practically implemented in quantitative models until recently. The aim of any predictive model for dissolution-controlled SCC is to identify the time windows in the loading history when these conditions are satisfied at sites where cracking occurs and then to integrate the time in these intervals. The amount of growth is simply the total time for cracking multiplied by the maximum cracking rate.⁵ The maximum rate could be calculated by Faraday's law or obtained as an empirical maximum rate.

A simple test that maximizes the time interval for cracking is the SSRT. This test tends to expose new surface through its duration, once the yield strain is achieved. For the materialenvironment systems dealt with, the observed maximum cracking rate from the SSRT was about 2.5×10^{-6} mm s⁻¹—or about a factor of 4 slower than the theoretical maximum rate based on Faraday's law. The SSRT has been used in Refs 11–13 as the empirical basis for the maximum cracking velocity.

The following section reformulates the displacement-controlled model of Ref 13 to deal with load control problems, with provision for creep and cyclic plasticity, such as may occur in TTT designed to simulate the service loading of transmission line pipe. The model is adapted for predictions of literature data for TTT specimens used to develop SCC threshold behavior for line-pipe steels in a carbonate-bicarbonate environment [16].

Similitude Conditions for Line-Pipe Steel Cracking in Carbonate-Bicarbonate

Electrochemical and Metallurgical Similitude

The electrolyte found in most SCC areas of natural gas line pipe in the United States and Canada is carbonate-bicarbonate; specifically a 1 N carbonate-1 N bicarbonate aqueous solution has been adopted as a test standard [16]. Susceptibility to SCC based on slow and fast scan potentiodynamic studies indicates that testing may be best done in the middle of the cracking range at about -650 mV SCE. Field observations of cracking locations indicate testing can be accelerated and remain representative at a maximum constant temperature of 75°C. In all cases, the initial pH should be 9.3.

The rate of cracking is considered to be proportional to the rate of bare-surface dissolution under this set of electrochemical parameters. Temperature is an implicit factor in that it influences at least the current density in Faraday's law—a result supported in practice by an Arrhenius type of behavior in cracking velocity as a function of temperature. It follows that cracking velocity can be calculated from Faraday's law or from empirical data with nominally continuous dissolution for the electrochemical conditions and the material of interest. Figure 1 shows empirical data derived from SSRT results that reasonably satisfy electrochemical and metallurgical similitude for the broad TTT database. Figure 1 presents average growth rates as a function of imposed strain rates from SSRT. Observe from this figure that cracking attributed to dissolution occurs at strain rates from about 10^{-8} /s to 10^{-5} /s. Figure 1 defines the window of strain rates for cracking, and the rate of cracking as a function of strain rate. The variation in cracking rate from the peak cracking rate at a strain rate of about 5×10^{-6} /s is attributed to differences in the time over which baresurface dissolution occurs—rather than differences in the maximum (instantaneous) rate of dissolution.

Mechanics similitude remains to be developed between the TTT specimen cycled at high

⁵ This idealization neglects the decay in rate associated with the repassivation process and so is reasonable so long as intervals of cracking are large compared to the repassivation transient decay time.



FIG. 1-Average crack speed as a function of strain rate for an X52 steel.

stress ratio (minimum stress/maximum stress) and the SSRT reference data before predictions can be made for the TTT database presented in Ref 16.

Mechanics Similitude

The SSRT provides an empirical calibration of the maximum dissolution (cracking) rate behavior for the material-environment system. The SSRT involves increasing displacement of the specimen over time for the duration of the test, with significant plastic deformation possible throughout the cross section. Figure 2 illustrates this tendency for an X60 steel in CO_3 -HCO₃ solution at 75°C for a range of potentials [17]. Observe that at -650 mV SCE,



FIG. 2—Nominal stress-time behavior of an X60 steel at 75°C in a carbonate-bicarbonate solution.

plastic flow continues well beyond the ultimate stress. At -650 mV these data show that deformation under increasing nominal stress lasts for about 10 h, with plastic flow beginning after about 4 h. Interrupted SSRT⁶ studies on X52 steel at -650 mV SCE and 75°C show a stress response similar to that in Fig. 2 over the interval of the test. These studies also indicate that noticeable cracking does not begin until inelastic action starts, and that average rates calculated once cracking begins do not vary significantly within a given test. When significant cracking occurs in the SSRT, a large number of cracks are observed to develop throughout the gage section that has been subjected to the imposed nominal displacement (strain) rate.

In contrast to the data in Fig. 2 for SSRT specimens, conditions producing cracking in TTT specimens include nominal stresses well below yield. Thus, the extent of plasticity is very limited in comparison with the SSRT, which provides continued elongation beyond the yield strain to sustain dissolution and, within the window of strain rates, avoids either complete repassivation or plastic flow outpacing of the dissolution. This difference in the extent of inelasticity that develops in the TTT as compared to the SSRT is thus a key to mechanics similitude. Differences in the type of loading—continued straining with rather uniform deformation in the test section in the SSRT versus high stress ratio cycling at nominally elastic mean or peak stresses in the TTT specimen, widespread cracking is observed similar to that observed in the SSRT specimen.

Metallurgical studies indicate that at free surfaces there is limited constraint to flow on slip-systems with a component normal to the free surface (for example, see Ref 18). This means that flow is enhanced at the free surface compared with the bulk behavior in the interior which, in turn, means that greater incompatibility would develop between surface grains than would occur in the bulk. For a dissolution-driven process that is kept active by inelastic action, this free-surface effect is significant. Crack nucleation, which occurs at grain boundaries at the surface, may develop due to surface enhanced incompatibility between grains when the bulk response, which is constrained by surrounding grains, is nominally elastic.

Experiments show that plastic flow in unconstrained crystals develops at stresses about a factor of 2 below that observed in constrained samples (surrounded bicrystals) (for example, see Ref 18). This free-surface effect dissipates as grain to grain compatibility develops, generally considered to occur within a 2 to 10 grain-deep layer. This means that plastic flow can occur in a near surface layer of a TTT specimen at nominal stresses as much as a factor of 2 less than the yield stress. Thus, it is possible for sustained grain-boundary dissolution to occur in the TTT specimen (as well as in the SSRT specimen) at stresses below the yield. The difference in the role of the free-surface effect between these tests is that the TTT specimen remains at nominally elastic stresses for which this free-surface effect is assumed to dissipate within 5 grains, whereas the SSRT continues to deform, with most of the cracking occurring with continued dissolution beyond the yield stress. Once the bulk yields, it is reasonable to assert that the surface-enhanced plasticity is not needed to support continued dissolution and, therefore, is no longer a factor for cracking in the SSRT specimen.⁷

Experiments also show that creep occurs at nominal stresses below yield at room temperature in C-Mn steels [13]. Figure 3, which shows isochronous stress-strain curves for an

⁶ The SSRT is stopped before fracture of the specimen occurs. This permits determination of when during the test cracking occurs and a more accurate estimate of the crack growth rate.

⁷ The mechanics aspects of free surface effects are emphasized herein. It may be also possible that surface condition is an issue for metallurgical-environmental similitude. Such has been avoided here by using specimens with mill surfaces removed but in general surface condition may be a significant issue.



FIG. 3—Normalized isochronous true stress-true strain behavior of X52 steel at 23°C.

X52 C-Mn steel, indicates such creep can occur well below nominal yield for the class of steels considered in prior TTT studies. The SSRT specimens support continued inelastic deformation to rather large stresses and strains, whereas the TTT specimens support cyclic loading at high mean stresses at near yield to nominally elastic levels. This difference in loading can cause differences in the time for dissolution due to creep at stresses near and beyond yield. The key difference is that the TTT specimen stays at or below yield stress levels so that possible creep deformation may support dissolution in this test. However, for SSRT tests creep is of little importance because the strains increase continuously under displacement control without evidence of load relaxation until the ultimate stress is achieved.

Finally, experiments also show that cyclic loading causes a transient stress-strain response, which in most X52 through X70 grades of line-pipe steel generally leads to cyclic softening (for example, see Ref 13). As shown by the stable cyclic stress-strain curve from an incremental step test [19] for a typical X52 in Fig. 4a, this cyclic softening leads to a reduction in the proportional limit as compared with the monotonic result that is developed in the SSRT. This means that cyclic loading, such as occurs in the TTT, can reduce the proportional limit below that observed in tension tests, so that the cyclically loaded TTT specimen may



FIG. 4—Cyclic deformation behavior of X52 steel at $23^{\circ}C$; (a) monotonic and cyclic stress-strain behavior and (b) stress response as a function of applied cycles.

experience plasticity that exposes fresh surface for dissolution at stresses below that experienced in the SSRT.

Observe in Fig. 4a that the reduction in proportional limit due to cyclic softening is significant—as much as a factor of 2. Thus, such softening could reduce the proportional limit in a TTT specimen to as much as a factor of 2 less than that of the SSRT specimen. Figure 4b reveals that the rate of this softening depends on the initial stress level and that

at low strains, such as are experienced in TTT specimens and in line pipes operating at 72%specified minimum yield stress (SMYS), this softening for this steel is delayed for thousands of cycles. This delayed softening means that a form of plasticity that may develop after years of service in line pipes-depending on the total cumulative plasticity-may never occur in TTT specimens tested over short time intervals (small cycle numbers). Figure 5 illustrates results for cyclic loading at a high mean stress. Figure 5a shows results for cycling at a maximum stress of 72% SMYS at 75°C, whereas Fig. 5b shows data for a higher maximum stress developed at 20°C. This figure shows that high stress-ratio cyclic loading like that in line pipes and that imposed on TTT specimens does develop a cyclic transient inelastic behavior that is consistent with the potential for both cyclic creep and softening based on the data presented in Figs. 3 and 5. Thus, the TTT specimen does develop inelastic action due to cyclic loading (see Fig. 5a) that exposes new surface and can support dissolution under loading conditions that are representative of actual service. Line pipe that experiences many more cycles than a TTT specimen in the typical seven-day test [16] could also experience delayed softening that may support dissolution that is otherwise excluded from both the SSRT and the TTT.

Modeling SCC Thresholds in the TTT

In order to use SSRT data as the basis to predict TTT SCC behavior, mechanical similitude between the two specimens must be satisfied. All forms of inelastic action due to differences in the loading, such as creep and cyclic softening, must be accounted for as must differences in the scale of inelastic action as presented in Fig. 5. Differences between the SSRT and the TTT due to loading and to the extent of inelastic action are evident in the experimental data shown in Figs. 2 to 5. The impact of the free-surface effect, which arises because of the differences in the extent of inelastic action, also must be accounted for. In this respect, both the TTT and SSRT specimens undergo unconstrained inelastic flow at the surface. In the SSRT, the monotonically increasing stress and strain levels eventually exceed the proportional limit of the material. When the specimen yields the free surface effect plasticity becomes insignificant compared with the gross plasticity throughout the cross section. The cyclic loading at all cross sections in the TTT does not, in general, approach yield upon each load reversal. In this case, the free surface inelastic strain is significant in the dissolution process.

The differences in the role of the free-surface effect between the TTT and the SSRT can be accounted for by a bimaterial model [13]. Differences in the loading in a SSRT and a TTT, which lead to additional sources of inelastic action for the TTT (creep, cyclic creep, and cyclic softening), could be accounted for through the constitutive response of the materials used in the bimaterial model.⁸

Bimaterial Model of Free-Surface Effect

For current purposes, the free-surface effect, which transitions smoothly from no constraint at the free surface to full constraint over 2 to 10 grains below the surface, is represented by a surface layer free of constraint on a core with full constraint. The surface layer, shown schematically in terms of mechanics boundary conditions in Fig. 6, is taken as 5 grains deep on a core that represents the remainder of the specimen. The grain size of the X52 steels

⁸ Much is made of inelastic components of strain whereas oxide rupture depends only on the strain increment over some time step. This emphasis arises from the fact that such contributions to the strain increment requires more than elastic considerations—nothing more is implied.


FIG. 5—Stress-strain behavior of typical X52 steels under service-simulation high stress ratio loadcontrolled cycling; (a) peak stress near maximum operating conditions at 75°C (longitudinal segment from pipe wall) and (b) peak stress near observed yield stress at 23°C (flattened strap from pipe circumference).





considered is about 25 μ m, so that the surface layer which is taken as 5 grains is 125 μ m thick. The specimen of interest is the full thickness of the pipe wall, typically about 5 mm, so that the two surface layers typically represent about 5% of the total wall thickness. The surface of the specimen is a patchwork of grains, each with local orientation and mismatch across grain boundaries. This patchwork continues randomly into the TTT specimen just as it does in the SSRT specimen, so that the in-plane mismatch strains caused by grain-to-grain compatibility are similar in metallurgically similar specimens for a given far-field stress. Empirical rates of intergranular or transgranular dissolution, therefore, can be applied from one sample to the next for the same set of mechanics conditions. It remains to account for the free-surface effect that modifies the far-field conditions imposed on the TTT specimen for the stress levels used in TTT [16].

The surface and core or bulk layers shown in Fig. 6 are represented as homogeneous isotropic materials whose stress-strain behavior can be represented in the form

$$e^{i} = e^{e} + e^{i} \tag{1}$$

where e^i , e^e , and e^i represent total, elastic, and inelastic strain, respectively. A power-law hardening response is assumed to relate stress, s, and e^i in the form

$$s = K(e^i)^n \tag{2}$$

where *n* is a hardening exponent and *K* is a strength coefficient found, respectively, as the slope and intercept at $e^i = 1$ from the best-fit of log *s* versus log e^i . The total strain in Eq 1, therefore, can be written with $E = s/e^e$ as

$$e' = \frac{s}{E} + \left(\frac{s}{K}\right)^{l/n} \tag{3}$$

When dealing with the bulk material behavior, the parameters K and n are subscripted b and found from full-wall thickness tests of pipe material. Values of K and n for the surface layer, subscripted s, have been determined from the observation that the flow stress for unconstrained material is greater than about 0.4 times that for constrained material, whereas the ratio of hardening rates is greater by about 2 times [18]. Specific values selected for the monotonic tension behavior of the bulk and corresponding surface values, consistent with this range, are: $n_b = 0.116$, $n_s = 0.20$, $K_b = 738$ MPa (107 ksi), and $K_s = 310$ MPa (45 ksi). The value of E is taken as 199.81 GPa (29 × 10³ ksi) for both the core and surface layer.⁹

For the TTT, the inelastic behavior characterized using the monotonic response must be modified by cycle- and time-dependent inelastic action, to the extent that it occurs in a test. For current purposes the time-dependent behavior is represented by the normalized isochronous stress-strain behavior for the X52 steel shown earlier in Fig. 3. Values for K and n are found as discrete functions of time by plotting the results in Fig. 3 on coordinates of log s and log e^i to develop K = K(t) and n = n(t). These functions are then made specific to the bulk or surface by multiplying the data in Fig. 3, which is normalized to yield stress, by the respective yield stresses. Cyclic creep is accounted for by time-stepping onto sequential isochronous stress-strain curves (see Fig. 3), with provision for the effects of memory for prior deformation such as is illustrated schematically in Fig. 7 and evident in actual test data in Fig. 5. Cycle-dependent softening can be characterized using the data shown in Fig. 5,

⁹ The effect of this choice of parameters is explored later.



FIG. 7—Simulated stress-strain response under high stress-ratio load-controlled cycling at a crosssection in a tapered-tension-test specimen; (a) nominal and surface layer response simulating loading conditions in a seven-day test and (b) detail from Part a indicating predicted paths with and without memory for prior plastic flow.

normalized with respect to yield stress as has been done in Fig. 3. The driving force for such softening is cumulative inelastic (cyclic plastic) strain, Σe^i , so that $K = K(\Sigma e^i)$ and $n = n(\Sigma e^i)$. Again, these cycle-dependent functions can be made specific to the bulk or surface by multiplying by the bulk and surface yield stresses, respectively. This approach assumes that creep and cyclic contributions to e^i are uncoupled. However, this is a moot point when the TTT cases considered represent seven-day tests at low frequencies with high mean stresses using material without a prior cyclic history. Even for the surface layer, the Σe^i over the period of the test on a virgin material does not lead to significant softening so this assumption never comes into play.

In Fig. 6, note that planes of symmetry are assumed in the direction of loading such that the taper of the TTT specimen is idealized for purposes of analysis, as a series of discrete prismatic sections. The boundary conditions that exist on this material element show equal displacement at the interface between the layers and through the thickness to satisfy the compatibility requirements. Variations in grain size can be accounted for in general by changing the relative thickness of the surface layer which for present purposes has been fixed at 125 μ m.¹⁰

The displacement that satisfies compatibility is a result of the stress distribution that develops in the two layers in response to the imposed load that is significantly different from the displacement controlled model [13]. Load control is simulated by specifying an applied load and requiring only that the total strain in both the surface and bulk layers remain equal. From Eq 3, this control condition can be written as

$$\frac{s_s}{E} + \left(\frac{s_s}{K_s}\right)^{1/n_s} = \frac{s_b}{E} + \left(\frac{s_b}{K_b}\right)^{1/n_b} \tag{4}$$

Surface and bulk stresses are functions of geometry (cross-section area), A, and load, P

$$s_s = f(A_s, P_s) \qquad s_b = f(A_b, P_b) \tag{5}$$

Details of the formulation and solution procedure are omitted for the sake of brevity. The stresses s_s and s_b have unique solutions that satisfy mechanical equilibrium as well as the compatibility imposed in Eq 4. Solving for the stresses allows straightforward calculation of both elastic and plastic strains using Eq 3.

In the TTT, load is applied as a sinusoidal function of time [16]. The model is numerically subjected to this sinusoidal load function, which is broken into discrete load-time steps for computational purposes. The strain and strain rates approach their instantaneous values as the load-time intervals approach zero, so that smaller time steps in some cases are needed for accurate solutions.

Time-dependent creep behavior is modeled by updating the inelastic strain parameters K(t) and n(t) with time. As seen in Fig. 3, when the stress in the specimen exceeds approximately 0.8 of the yield stress, the material deforms inelastically by creep. At each load step, the stress level is checked and K(t) and n(t) are updated accordingly. This effectively allows the model to accumulate inelastic time-dependent strain as seen schematically, for example, in the predicted ratcheting behavior shown in Fig. 7a. Figure 7b illustrates that with each reloading the material has a "memory" of prior plastic flow, which for the present formulation is based on a kinematic hardening framework. The term "memory" relates to the tendency of a material to recognize the prior maximum strain in its history, at which point the deformation path shifts from a continued extension of the current path onto the

¹⁰ The effect of choosing this parameter is explored later.

prior path as shown in Fig. 7b. The creep strain is added to the plastic strain to determine the total inelastic strain accumulated during the load step. The inelastic strain rate is found by dividing the total inelastic strain by the time interval of that load step. Note that both ratcheting and memory illustrated schematically in Figs. 7a and b can be seen in actual tests of pipe steel for near-service load histories, as is evident in Figs. 5a and b.

The strain and inelastic strain rate for both the surface and bulk are calculated at each load step to determine if the conditions for continued bare-surface dissolution are satisfied. The maximum crack growth, as determined empirically from the SSRT data, is then used to calculate the increase in crack length over the time step. While the crack grows through the surface layer, the surface strain and inelastic strain rate are used to determine the cracking rates.¹¹ Continued cracking into the bulk requires satisfying the conditions for cracking in the bulk layer. Failure to achieve these conditions leads to predictions of arresting (non-propagating) cracks.

Predicting the Cracking Behavior of TTT Specimens

The cracking behavior of TTT specimens is reported in Ref 16 as a threshold to form cracks, which is a function of maximum stress, stress range, and frequency for the material and environment of interest. The threshold was defined as the stress below which the three deepest cracks, intersected along a longitudinal centerline section, fail to grow more than 0.01 mm.¹² Figure 8*a* presents typical experimental data for a single test in terms of observed crack length as a function of position along the taper. The threshold stress is the load divided by the cross-section area at a crack depth of 0.01 mm. Figure 8*b* is the crack depth predicted as a function of stress associated with specific cross sections along the tapered specimen for the same test conditions presented in Fig. 8*a*.¹³ As in Fig. 8*a*, the threshold stress is found by dividing the imposed maximum load by the cross-section area at the position along the taper for which the threshold crack depth develops. For the case shown the predicted and observed thresholds match very closely. Figure 8*c* presents the threshold stress obtained from results such as shown in Fig. 8*a* for observed data and Fig. 8*b* for predictions, plotted

¹² For present purposes, the raw-data of Ref *16* have been reanalyzed with the threshold defined as the stress below which a crack intersected along a longitudinal centerline section failed to grow more than 0.01 mm. Reanalysis was prompted by the fact that a single section would not find all cracks that exist at a given stress nor will it necessarily cut a crack at its deepest point. As such, the experiments represent an upper-bound threshold when compared to predictions. A more realistic threshold would be found by a statistical model that recognizes and accounts for the unique features of the test method reported in Ref *16*.

¹³ Crack depth is often predicted to be less in areas of high stress. As discussed later, crack growth for the conditions discussed seems to be controlled by primary creep, which at higher stresses may saturate quickly by hardening to elastic behavior, with strain increments less than that needed to cause film rupture. Therefore, the time for crack growth is less or the minimum strain for rupture is not achieved, respectively, consistent with the observed decrease in crack depth at higher stresses.

¹¹ As presented in this paper, the model does not explicitly account for notch and singular effects that develop as the SCC crack penetrates the surface and continues into the bulk. Notch effects have since been included through a Neuber notch analysis, as is commonly used in fatigue crack nucleation studies (for example, see Ref 20). Consideration has likewise been given to singular effects through inelastic adaptations of the linear elastic stress intensity factor (for example, see discussion of adaptations in Ref 21). Finally, the sister form of this analysis for inelastic analysis of macroscopic crack growth [11] has been used to assess the significance of crack depth. Details of these considerations are beyond the scope of this paper. Suffice it to note here that analysis for macroscopic cracks indicate that the singular effect of the crack is to ensure that conditions related to the maximum strain for cracking are almost always satisfied: the condition for continued cracking, therefore, is largely set by local strain rates. Approximate analysis for commonly used nominal stressing rates and TTT conditions.



FIG. 8—Comparison of observed and predicted cracking behavior along the taper in a typical taperedtension test (360 MPa maximum stress and a 73 MPa range): (a) observed response based on a centerline section where threshold = 251 MPa; (b) predicted response where threshold = 254 MPa; and (c) comparison of data and predictions for a wide range of test parameters.

as a function of stress range. The data in Fig. 8c represent four frequencies, f, in the interval $3.33 \times 10^{-6} \le f \le 3.33 \times 10^{-3}$ hz and maximum stresses from less than to just above the 0.5% strain yield stress of the steel.

Predicting the threshold behavior shown in Fig. 8b and in summary in Fig. 8c involves predicting the cracking behavior for each combination of frequency, f, maximum load, P_{mx} , and load range, ΔP , shown for discrete cross sections along the taper for each combination of loading parameters. This is done by solving Eqs 3 and 4 for the case where the surface layer is 125 μ m thick, which defines A_s , A_b in Eq 5, and for small time steps in the load history, $P = P_o + P/2 \sin (2 \pi ft)$ where t is time and f is frequency. Time steps must mutually satisfy the following conditions for cracking to occur:

- (1) $10^{-8} \ge \dot{e}_s^P \ge 3 \times 10^{-4} \text{ s}^{-1}$: continued dissolution, controlled by strain rate, where \dot{e}_s is the surface strain rate,
- (2) $s_s \ge 0.8 \ s_{ys}$: onset of inelastic action (film rupture) for creep, herein controlled by bulk creep; $s_b \ge 0.8 \ s_{yb}$, where s_b is the stress in the bulk and s_{yb} is the yield stress in the bulk, and
- (3) $e_s^{P} \ge 0.02 \ e_s^{T}$: onset of inelastic action (film rupture) for cyclic component of the loading.

These conditions are derived from Figs. 1, 3, and 4 as are the parameters for Eq 3.¹⁴ Crack advance in each step is found by multiplying the time over that step by the corresponding cracking rate obtained from Fig. 1. The total crack advance is then the running sum of crack advance over the life of the test. For conditions below the threshold only a few time steps in the loading history admit cracking, whereas portions of the TTT specimen well above the threshold show a significant time interval for cracking. It is significant that, at the value of \dot{e}_s^P for maximum cracking rate ($\leq 2 \times 10^{-6}$ mm/s), growth for only 1.39 h is needed for a crack to grow to the threshold depth. That is, for a seven-day test the threshold condition is exceeded if crack growth is active under optimal conditions during less than 1% of the total test time.

Loading conditions for which cracks grow beyond the threshold depth permit determining the threshold as a function of maximum cyclic stress and frequency. A range of frequencies from 0.2 min^{-1} to 0.0002 min^{-1} have been explored experimentally at maximum cyclic stress ranges from 10 MPa through 100 MPa at stress ratios from 0.02 to 0.30. Thresholds determined from crack measurements made along the centerline of the specimen are plotted over this range of conditions in Fig. 8*c* and are represented by various symbols. Figure 8*c* also shows the predicted threshold behavior of these specimens representing the extremes of the frequencies tested. These predictions indicate a weak frequency and stress range dependence. Figure 8*c* shows that the predictions lie near a lower bound compared with actual test data.

Study of the trends in the test data show the same weak dependence on frequency and stress range, but also show significant scatter in the threshold stress. According to the predictions, the maximum stress in the loading history controls the time interval over which creep occurs, which in turn controls the time over which inelastic action admits cracking. Maximum stresses well over the threshold for creep ($\sim 0.8 \ s_{yb}$) produced cracking over significant time intervals so that the threshold depth developed early in the seven-day test, at maximum stresses up to about 400 MPa. At higher maximum stresses the time interval required to saturate creep was predicted to decrease, such that the time for which inelastic

¹⁴ The specific constants in these equations are material-environment specific. Other steels in a carbonate-bicarbonate environment indicate the constant in Condition (2) may go as low as 0.6, suggesting that differences exist in the isochronous stress-strain curves at small strains for line pipe steels.



FIG. 9—Dependence of predicted threshold for typical tapered-tension test conditions on the parameters selected to implement the model.

action that sustained SCC consistent with Condition (2) is predicted to decrease. Model predictions thus imply an interesting critical test case: a very high maximum stress coupled with a stress range with limited cyclic plasticity could fail to develop the threshold crack depth in a seven-day or shorter-duration test. This is consistent with data in Fig. 3, which implies creep saturates quickly at high stresses. Analysis indicates that cracking can be limited to less than the threshold depth by saturating creep quickly using a maximum stress of 482 MPa (about 94% of the ultimate stress). Figure 4b implies that this maximum stress could be coupled with a stress range of about 69 MPa without much concern for cracking due to cyclic plasticity.

Figure 9 presents the experimental results developed for this critical test case in terms of crack number as a function of position along the taper. Note that in the area of high stress no cracks are observed, but that cracks deeper than the threshold are found further down the taper. While not conclusive in demonstrating the validity of the present model, such trends indicate the utility of models in identifying conditions that are either prone to or that avoid SCC susceptibility.

Discussion

The model appears to be consistent with the threshold cracking behavior for line-pipe steels in a carbonate-bicarbonate environment based on results for TTT specimens. The predicted and observed trends match well over the range of parameters studied. For the seven-day test, predicted trends for cracking seem to be controlled by the monotonic creep behavior. The ratcheting (shown in Fig. 7a) that occurs in the ensuing cycles has been reasonably accounted for by time-stepping onto sequential isochronous stress-strain curves. Consequently, the threshold for cracking in these short-term tests appears to be controlled by creep behavior, such as that shown in Fig. 3.

Model predictions for a short-term TTT, such as a seven-day test, show only a limited dependence on the free-surface effect (as provided with reference to Fig. 6 through Eqs 3

to 5). This occurs for two reasons. First, under creep conditions the compatibility requirement between the surface and the bulk means that the free surface cannot creep without creep in the bulk. The bulk creep response therefore is the first-order factor controlling the evolution of inelastic strain and the related SCC in the seven-day TTT. Second, the TTT uses a high mean stress that in line pipe steels exceeds these materials resistance to creep, with sufficient inelastic cyclic strain accumulated over the seven-day test to promote SCC and develop the threshold crack depth. (Recall that for cracking at the maximum theoretical rate the "threshold" crack depth develops in less than 1% of the time available in a seven-day test.) Thus, for many line pipe steels the threshold is controlled by bulk creep, which may limit the utility of the test when used in this manner.

It follows that test data for conditions other than a seven-day test, which emphasize or discriminate secondary creep effects, the role of cycles, and admit the related free-surface effect, are necessary to assess the more general potential utility of the model.¹⁵ These test conditions could involve longer-term tests that provide for cyclic softening of virgin material. Alternatively, shorter-term tests of preconditioned material, which has been cyclically softened prior to environmental exposure, could be employed. Such a test would explore the possibility that delayed softening, such as shown in Fig. 4b, could create plasticity that promotes SCC long after the line is commissioned—a possibility that cannot be explored in the standard seven-day test protocol.

Provided that this short-term creep behavior controls SCC in the field, the seven-day TTT is a viable tool to screen susceptibility for service. The results that underlie Fig. 4 imply that measurable primary creep saturates a little beyond 10⁵ s at the lowest stresses and earlier at higher stresses. The literature indicates that SCC does not occur unless samples are exposed to the environment when this creep is active [3]. It follows that unless the environmental parameters are present when the line pipe is commissioned, it is unlikely that such short-term creep can be solely responsible for line pipe SCC. Likewise, from a rigorous academic view, it is not clear that SSC susceptibility of a line pipe that develops cracking long after the line is commissioned can be characterized by the TTT when short-term creep controls the cracking process.¹⁶ Despite this, there is reason to suggest that a short-term, creep-dominated test may actually produce data useful in assessing susceptibility even when the inelastic action generating new surface area for dissolution is developed by other long-term mechanisms like cyclic softening. The amount of inelastic action due to short-term primary creep is controlled by (1) the onset of inelastic action that can be measured in terms

¹⁵ The mechanics of free-surface effects would in general depend on the loading. Creep under tension would not admit as much surface deformation as would reversed plasticity due to cyclic loading that is known to cause extensive surface plasticity.

¹⁶ That TTT samples cut from steel lines that have been in service for many years develop cracks seems to conflict with this assertion. Note, however, that TTT samples are cut from such lines in the longitudinal direction or from flattened blanks cut in a circumferential orientation. In the case of longitudinal samples, the service stress history in this direction represents low levels as restrained pipe has only Poisson-induced longitudinal stresses. As such, longitudinal specimens represent a near-virgin material state at near yield stress levels and thus have the same potential for short-term creep after service that they had at the start of service. Such samples should and do show a susceptibility to SCC after service that is very similar to that for comparable steels tested prior to service, if their surface conditions are similar. For samples cut from flattened straps, the stress-strain history associated with flattening creates the potential for redistribution of stresses upon reloading of the strap as in a TTT specimen. Cracking susceptibility in such cases would not be surprising, and would be difficult to relate solely to the service condition. (Other test types that show SCC susceptibility for samples removed from service and tested in a circumferential orientation involve either (1) stress levels that are in excess of service or (2) stress redistribution due to loadings that create stresses other than the membrane tension seen in service. Short-term inelastic action is to be expected in such cases so cracking would not be surprising.)

of the ratio of the imposed stress level to the proportional limit, and (2) the time interval over which inelastic action occurs that is set by the rate of (strain) hardening. That is, the amount of inelastic action due to short-term creep is determined in large part by the shape of the monotonic stress-strain curve. The amount of cyclic softening is also keyed to the shape of this curve. Therefore, if two different steels had similar rates of cyclic softening, it is not unreasonable to expect that their SCC susceptibilities in long-term cyclic loadings would parallel the trends determined by short-term tests. Time dependent changes in the surface, such as significant pitting, could, under certain conditions, also lead to inelastic action well after a line is commissioned.¹⁷ It follows that short-term tests may serve as an indicator of SCC susceptibility in these cases too. However, using the results of seven-day TTT to predict line-pipe SCC susceptibility may in these cases, as well as in cases involving cyclic softening, be quite complicated if not impossible.

As in all models of a physical process, the present model makes use of material constants and other parameters to make the model application specific. For the present model, these constants enter through Eqs 4 and 5. As discussed earlier, the values selected for these constants represent actual test data directly or indirectly. The three constants that involve the greatest uncertainty or latitude in their selection are associated with the surface layer. These constants are (1) the hardening coefficient, (2) the hardening rate, and (3) the thickness of the surface layer. For test conditions that reflect a creep controlled situation, such as the seven-day TTT, the trends in Figs. 10a and b show that the hardening behavior has only a modest influence on the threshold for SCC over a quite broad range, thereby covering the practical limits of the first two parameters. The values selected for the hardening parameters lie near the middle of this practical range that is represented by the range of values explored in Figs. 10a and b. Other values could be selected without strongly changing the trends presented, as is evident from these two figures.

In contrast to the relative insensitivity to hardening characteristics, the thickness of the surface layer shows a possibly strong influence on threshold stress, as evident in Fig. 10c. This is because the thickness of this layer controls the balance of stresses between the layers (Eq 4). Thus, the thickness of the surface layer exerts a direct effect on the time during the loading that $s_b \ge 0.8 s_{yb}$ (Condition 2), which in turn controls the crack depth achieved along the taper in the TTT specimen. The literature discussed in regard to free-surface effects would admit thicknesses from 2 to 10 grains. As such, the strong dependence of threshold possible within the trend of Fig. 10c cannot develop since practical considerations limit its range to values within several percent of the value calculated and discussed earlier. It follows that the values for the constants selected in implementing the model do not strongly influence the predictions presented and thus do not alter the practical implications.

Summary

A model for SCC crack initiation and early growth has been developed and used to rationalize the SCC behavior observed in tapered-tension tests (TTT) of line-pipe steels that have been tested under high maximum stress levels with a small amplitude controlled cyclic component in a carbonate-bicarbonate environment. Results presented indicate a good correlation between the observed susceptibility and that predicted with the model. Results developed for the slow-strain-rate test were used as the independent calibration data that

¹⁷ Other surface-related factors may also be important. For example, tight continuous mill-scale is observed to be protective at least in short-term tests at moderate stress levels. In contrast, seasoned surfaces that have discontinuous mill-scale or pits appear to be deleterious. General models useful in practical applications would have to reflect these factors.



FIG. 10—Observed cracking behavior for a tapered-tension test at a maximum stress of 482 MPa and a range of 69 MPa: (a) hardening coefficient, (b) hardening rate, and (c) thickness of surface layer.

when coupled with a strain and strain-rate based analyses of the loading history of the tapered-tension test provided (1) when in the loading history cracking occurred and (2) the cracking kinetics to permit predictions of crack depth and therefore threshold stress. Comparison of predictions with test results showed that predictions closely matched observed results from the already published database as well as the data developed to test predictions for discriminating blind experiments.

Conclusions

The main conclusion is that models of SCC can be used to rationalize experimentally observed cracking behavior and as such can be used to identify conditions for cracking or mitigation beyond the scope of laboratory experiments. It is possible that such models can provide the basis by which to judge how changes in material, operating conditions, or environment influence the service performance of practical systems such as line pipe. Such models can also provide guidelines for streamlining future experimental programs by identifying critical test conditions.

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A Model for Environmentally Assisted Crack Growth Rate

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ABSTRACT: A superposition model for corrosion fatigue formulated for reactor pressure vessel (RPV) steel is described in this paper. The three components of crack growth rate are associated to pure fatigue, true corrosion fatigue, and stress corrosion.

The true corrosion fatigue behavior can be correlated with the material properties with regard to the resistance to generalized corrosion: the stress corrosion behavior can be correlated to the stress corrosion susceptibility of the material/environment couple.

While in pure fatigue and true corrosion fatigue the crack growth rate is depending on the applied ΔK (following Paris law), the stress corrosion component is time dependent. The onset of the stress corrosion component is associated with a critical ΔK (ΔK_c), whose is depending on frequency.

The meaning of ΔK_c is discussed and compared with the classical stress corrosion parameter K_{ISCC} .

The good prediction obtained for RPV steels suggests to extend this approach to other materials; an application to AISI 304 stainless steel is proposed.

KEY WORDS: fatigue (materials), cracking, environmental effects, corrosion fatigue crack growth rate, stress corrosion, fatigue striations, pressure vessel steels, sensitized stainless steels

One of the main goals of research in environmentally assisted fatigue cracking is to develop the capability of predicting, for design purposes, the maximum crack growth rate that can be expected under a particular set of environmental conditions. To obtain a good prediction, quantitative understanding of the mechanism involved is essential.

Several parameters influence crack growth behavior of materials in aqueous environment, some of them being dependent on the material properties and some on the water chemistry characteristics. To understand the role of each parameter, a simple superposition model can be helpful.

A linear superposition model has been first proposed in 1969 by Wei and Landes [I] who assumed that the enhancement of crack growth rate due to the presence of environment results from the sustained load contribution. However, the load-environment interaction is better described by a three-component model [2,3], which are: (a) a mechanical component, associated with inert environments, (b), a ΔK -dependent environmental component, and (c) a time-dependent environmental component. The time-dependent mechanism is due to the sustained load contribution, can be treated as stress corrosion cracking, and can account for the effect of frequency [4]. Moreover, the two components can be associated with two

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different corrosion fatigue mechanisms, each one producing a different fracture surface appearance [5]. The main purposes of this paper are:

- (a) to quantitatively describe the approach that permits the calculation of the maximum possible fatigue crack growth rate in environment;
- (b) to compare the time dependent component (stress corrosion component) with results of stress corrosion cracking (SCC) tests; and
- (c) to show the evidence of the described behavior for different material-environment couples.

Corrosion-Fatigue Crack Propagation Mechanisms

The three-component model is schematically shown in Fig. 1. The crack growth rate versus ΔK plot for a metal in an inert environment follows Paris law (at ΔK above the threshold value). The presence of an aggressive environment causes an increase in crack growth rate that can be due to true corrosion fatigue (TCF) (Fig. 1*a*), with crack growth rate still following Paris law, or can be due to stress corrosion (SC), introducing a plateau-like component (Fig. 1*b*).

Both components can be present, as shown in Fig. 1c.

As already mentioned, the TCF component is assumed to be associated with a da/dN versus ΔK plot that follows the Paris law. Experimental results [6] do confirm that, when only this component is present, little or no time base effects are noticed on crack growth rate. For instance, frequency effects are negligible as for air data. The SEM examination of fracture surfaces reveals features usually indicated as "ductile" [7], very similar to fracture surface of specimen tested in air.

The SC component introduces a plateau-like behavior in the da/dN versus ΔK plot. The



FIG. 1—Schematic of corrosion fatigue processes, taken from Ref 2.

plateau cyclic crack growth rate increases as the loading frequency is lower [6]; as ΔK increases, the SC component is almost constant, until it equals the TCF crack growth rate at the same ΔK value, and the plot follows again the Paris law [8] (Fig. 1c).

Stress corrosion specialists have shown a similar plateau on da/dt versus K plot, during tests performed under constant loading on precracked specimens [9].

Quantitative Approach to the SC Component

In order to quantitatively compare data obtained under monotonic and cyclic loading conditions, the da/dN measurements must be converted to time base crack growth rate. During this conversion, it is assumed that:

- 1. The crack is propagating only during the loading part of the cycle period (T).
- 2. The increment in crack advance per cycle, due to stress corrosion and to true corrosion fatigue effect, are mechanistically independent and the absolute amount of the stress corrosion component can be evaluated by subtracting the TCF component from the total crack advance per cycle observed in environment.

Thus, the SC component of the average crack growth rate during each loading period at a given ΔK can be calculated as follows

$$\frac{da}{dt_{\rm SC}} = \left[\frac{da}{dN_{\rm tot}} - \frac{da}{dN_{\rm TCF}}\right]/T \tag{1}$$

As the involved mechanism is the same that is active in stress corrosion, the value of $(da/dt)_{SC}$ is expected to be the same as the plateau value of da/dt measured during stress corrosion tests, and to be constant in a range of ΔK . It has been found, however, that the ΔK value corresponding to the onset of the SC component during fatigue is dependent on the loading frequency [6,8], while for constant load tests, a unique value of K_{ISCC} for a given material environment couple can be determined [9].

In the following, a rationale for the dependence of threshold values on frequencies during fatigue is proposed based on

- 1. The existence of a particular range of active surface creation rate (ASCR) values promoting SC phenomena.
- 2. The dependence of ASCR on loading parameters.

Critical ΔK for the SC Component

The range of ASCR values promoting SC phenomena depends on the passivation rate of the examined ductile alloy in the selected aqueous environment. As schematically shown in Fig. 2, if the active surface is created at a rate much lower than the passivation rate, only a small amount of metal removal occurs, before oxidation (Fig. 2-I Case). Vice versa a too fast ASCR gives rise to a blunt crack (Fig. 2-III Case).

A sharp crack can be formed only when the active surface is created at a rate, which is comparable to the passivation rate (Fig. 2-II Case).

For a smooth specimen tested under strain control, ASCR is a function of the applied strain rate. Actually, it is well recognized that a critical strain rate is required to obtain significant SCC in ductile alloy/aqueous environment systems.



FIG. 2—Schematic of the formation of a stress corrosion crack, as depending on active surface creation rate and passivation rate (Ref 11).

For a notched specimen, it can be assumed that the active surface region at the crack tip is proportional to the stretch zone, which in turn is comparable with crack tip opening displacement (δ). In the case of small scale yielding, the crack tip opening displacement is

$$\delta = \frac{K^2}{\sigma_{\rm Y} E} \tag{2}$$

where

E = elastic modulus and σ_{γ} = yield strength.

During a fatigue test since the stress-intensity factor is a function of time, the mean δ value on the single cycle can be calculated, as follows

$$\delta = \frac{1}{T} \int_{\delta_{\min}}^{\delta_{\max}} d\delta \tag{3}$$

Since during a cycle the δ increment due to crack growth is negligible

$$\dot{\delta} = \frac{1}{T} \left(\delta_{\max} - \delta_{\min} \right) \tag{4}$$

The initial assumption that in a notched specimen, during fatigue the active surface creation rate is proportional to δ leads to

$$ASCR = \alpha \cdot \frac{1}{T} \left(\delta_{\max} - \delta_{\min} \right)$$
(5)

Substituting Eq 2 and the interrelationships between K_{max} , K_{min} , ΔK , and R ratio in Eq 5, it follows that

$$ASCR = \alpha \cdot \frac{1}{T\sigma E} \cdot \Delta K^2 \cdot \frac{1+R}{1-R}$$
(6)

It can be assumed that the onset of the stress corrosion component will occur when ASCR is comparable to the stress corrosion crack growth rate for the environment/material system considered.

Substituting $(da/dt)_{sc}$ to ASCR in Eq 6, ΔK_c is found to be

$$\Delta K_{\rm C}^2 = \frac{1}{\alpha} \cdot \sigma_{\rm Y} E T \cdot \frac{1-R}{1+R} \frac{da}{dt_{\rm sC}}$$
(7)

where ΔK_c is different from K_{ISCC} as obtained from constant load testing; in particular, it is inversely proportional to the loading frequency, so that a different ΔK_c can be calculated for each test frequency.

Limit Curves

The maximum expected crack growth rate, for a material-environment couple susceptible to stress corrosion cracking, can be calculated as

$$\frac{da}{dN_{\rm max}} = \frac{da}{dN_{\rm TCF}} + T \frac{da}{dt_{\rm SC}}$$
(8)

1. $(da/dN)_{TCF}$ is an exponential (Paris law), which has the equation

$$\frac{da}{dN_{\rm TCF}} = A \cdot \Delta K^n \tag{9}$$

The two parameters A,n depend on the material and environment characteristics; in particular, the susceptibility to true corrosion fatigue is related to the susceptibility to generalized corrosion, and is expected to be different at different temperatures;

2. $(da/dt)_{sc}$ is almost constant, and can be estimated also from Slow Strain Rate Tests (SSRT) results. This component is present only when the applied ΔK is larger than ΔK_c , which is a function of frequency. The value of $(da/dt)_{sc}$ depends also from the material environment couple, following its stress corrosion behavior.



 ΔK

FIG. 3—Limit curves for a material susceptible to both generalized corrosion and stress-corrosion cracking, for three different frequencies (f_0, f_1, f_2) .

Figure 3 shows schematically the limit curves for a material susceptible to both generalized corrosion and stress corrosion cracking, for three different frequencies $(f_0 > f_1 > f_2)$. The crack growth rate due to true corrosion fatigue is higher than the crack growth rate in inert environment; the stress corrosion component is time-dependent: as a consequence, the plateau position is higher when the frequency is lower.

Different material-environment couples have different behaviors both at corrosion and at stress-corrosion. For each of them a different family of limit curves can be determined on the basis of the proposed model and experimental results. This will be made in the following, using actual data, for two nuclear steels.

Pressure Vessel Steel

Since 1980, the corrosion fatigue behavior of A533B in reactor grade water at 288°C has been studied at CISE [12,13] in the frame of a program sponsored by the Italian Electricity Board-Research and Development Division (ENEL-DSR). A533B pressure vessel steel is

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FIG. 4—Ductile fracture surface morphology of A533B steel.

a low alloy bainitic steel, susceptible to generalized corrosion in water at 288°C [14]; moreover, Speidel has found stress corrosion cracking susceptibility in water environment [15]. It has been demonstrated [16] that the SC component is due to the presence of sulfur (S); both sulfur percent by weight and size, shape, and orientation of the manganese sulfide (MnS) inclusions seem to be important [17]. As a consequence, this material is expected to conform to the situation shown in Fig. 1c, where both components are present. For a quantitative approach, it is necessary to separate the two components.

A ductile fractographic appearance is coupled with true corrosion fatigue as shown in Fig. 4; when the surface is ductile all over the crack front for a macroscopic crack increment, the corresponding values of da/dN, ΔK have been calculated. Such values, taken from different tests [8], have been used to calculate the "ductile base line" having the equation

$$\frac{da}{dN_{\rm TCF}} = 3.41 \times 10^{-8} \cdot \Delta K^{2.575} \,(\rm mm/cycle)$$
(10)

In Fig. 5 this line is shown, compared with the ASMEXI code line for air tests, and with the summary of air tests at 288°C from the ICCGR (International Cyclic Crack Growth Rate) Group data base. Ductile striation spacings, *Sd*, have been measured at a $\Delta K > 50$ MPa \sqrt{m} [18]; the obtained values are in good agreement with the crack growth rate (Fig. 5). The comparison with the Paris law calculated in air at 288°C for pressure vessel steel [19] shows that the crack growth rate is higher in water than in air.

Equation 10 has been verified by results obtained on a specimen containing very low sulfur (0.004%) (Fig. 6). No effect of frequency has been seen. The agreement between the ductile base line and the low sulfur data (Figs. 5 and 6) is quite good.



FIG. 5—"Ductile base line" obtained for A533B steel and measured values of ductile striation spacing (dots).

To separate the SC component, Eq 1 can be used. (The TCF component has the same equation as the ductile base line). The results for A533B in 288°C water indicate a crack growth rate of about 10^{-4} mm/s. During fatigue, the presence of the SC component gives rise to the formation of brittle striations, whose spacing S_b is frequency dependent [18], as shown in Figs. 7 and 8. The brittle striation spacings (transformed to a time base) have a good correlation with the SC crack growth rate of 10^{-4} mm/s, as shown in Fig. 9.



FIG. 6—The da/dN versus ΔK plot for a very low S (0.004%) A533B steel.

The same value has been found [15] during constant load tests on pre-cracked specimens, with no dependence on the oxygen content in the testing environment.

Including a quantitative estimate of both SC and TCF components, the maximum expected crack growth rate can be calculated as follows

$$\frac{da}{dN_{\rm max}} = 3.41 \times 10^{-8} \cdot \Delta K^{2.575} + 10^{-4} \cdot T(\rm mm/cycle)$$
(11)

Equation 11 gives an estimate of the maximum crack growth rate that can be expected at a given test frequency; however, this estimate becomes far too conservative at low ΔK , if one assumes that the SC component is active independently from ΔK . Obtained results



FIG. 7—Brittle striations observed on A533B steel tested at different frequencies: 0.033 Hz (top), 0.017 Hz (middle), 0.0017 Hz (bottom) (see ink markings).

show that, to observe the SC component, ΔK must exceed a value (ΔK_c) which is inversely proportional to the frequency.

Results from several tests made at CISE are shown in Fig. 10; the comparison with the maximum expected crack growth rate (calculated by Eq 11) is quite good; the presence of ΔK_c is clearly indicated.

The correspondence with the model has been verified previously in other laboratories data [8].





FIG. 8—Frequency dependence of S_b (full symbols) and comparison between S_b and da/dN versus ΔK plots (open symbols).



FIG. 9—Comparison between S_b transformed in a time base (symbols) and experimental (---) and maximum (----) values of $(da/dt)_{sc}$.

Stainless Steel

The AISI 304 austenitic stainless steel is very little susceptible to generalized corrosion in water environment; it is susceptible to intergranular SCC when sensitized. As a first approach, the material has been considered as following the behavior shown in Fig. 1c. At the temperature of 288° C, the crack growth rate in air has been calculated by Bernard and Slama [20]

$$\frac{da}{dN} = 7.5 \times 10^{-10} \cdot \Delta K^4 \text{ mm/cycle}$$
(12)



FIG. 10—Comparison between the limit curves of the model and CISE results for A533B steel at different frequencies.



FIG. 11-Plot of da/dN versus ΔK for a not sensitized AISI 304 stainless steel.

The $(da/dt)_{sc}$ data obtained on pre-cracked specimens have shown a dependence on oxygen content; in oxygenated water (8 ppm) the crack growth rate is about 2.5×10^{-6} mm/s, as found at CISE² and by Speidel [15].

Preliminary tests have been made on unsensitized material; in this case, no frequency effect was seen, and the crack growth rate was similar to the air crack growth rate at the same temperature (Fig. 11), confirming that the generalized corrosion component for this material in pure water is small. The fracture surface shows ductile morphology (Fig. 12). Other authors have shown, however, that when an SCC component is present, as for instance in a sensitized steel, a plateau-like crack growth rate is obtained, associated with an intergranular fracture surface [22].

The position of the plateaus in the da/dN versus ΔK plot can be predicted from the knowledge of $(da/dt)_{sc}$. Figure 13 shows a family of limit curves for stainless steel, calculated by using the $(da/dt)_{sc}$ value corresponding to oxygenated water.

² Unpublished work supported by an ENEL-DSR research program.



FIG. 12—Ductile fracture surface morphology of a not sensitized AISI 304 stainless steel (Fig. 11).

The estimate of ΔK_c for stainless steel requires further work; this quantity should be lower than for A533B, due to the lower $(da/dt)_{SC}$ and to lower σ_Y of this material. The frequency dependence is supposed to be similar for both materials.

Conclusions

The three components superposition model described in this paper permits the prediction of corrosion fatigue test results on the basis of corrosion and stress corrosion data. On a qualitative basis, the TCF component can be correlated with the generalized corrosion resistance of the material; on a more quantitative basis, the maximum fatigue crack growth rate has been shown to be related to the stress corrosion crack growth rate, which can be measured during stress corrosion tests on precracked specimens.

The concept of K_c has been presented; this quantity can be related to K_{ISCC} , but has different values, due to the difference in loading between fatigue and constant load tests. Its dependence on frequency has been confirmed by experimental results.

The extension of the model, first made on reactor pressure vessel steel, to other material environment couples can be useful for predicting the behavior of the materials under corrosion fatigue.

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FIG. 13—Limit curves for stainless steel obtained from the ductile base line of Fig. 11 and the $(da/dt)_{sc}$ value corresponding to oxygenated water (T = loading part of the cycle period).

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Modeling of Sulfide Inclusion Distributions in Relation to the Environmentally Assisted Cracking of Low-Alloy Steels in a Pressurized Water Reactor Environment

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ABSTRACT: Work carried out in the recent past by members of the International Cyclic Crack Growth Rate Group (ICCGRG) has demonstrated the close connection between the occurrence of environmentally assisted cracking (EAC) in low-alloy steels in a pressurized water environment and the presence of sulfide inclusions in the steel. Due to the length of time that experimental work can take, coupled with the sometimes poor repeatability of tests, work was undertaken on a computer model of "sulfide particle" distributions and their interaction with a hypothetical crack front.

The model is basically simple in concept, proceeding in the following manner. An array of randomly located spherical particles, each assumed to consist of a large number of subparticles is set up within a matrix. A crack, exposed to a water environment, is then grown through this matrix, particles intercepted by the crack dissolving; this is modeled by the spreading out of subparticles. Additional factors such as the rate of particle dissolution and rate of subparticle loss from the system are also incorporated into the model. The model is set up to calculate the number of subparticles that congregate at the crack tip. The single premise adopted is that greater than a specified number of subparticles at the crack tip is sufficient to bring about EAC.

In the work discussed here, consideration is given to the relative importance of material sulfur content and second-phase particle size. It was found that the latter had a much greater influence on subparticle numbers at the crack tip than the former. From this, it is concluded that the setting of a bounding curve in Section XI of the ASME Code for modern low sulfur steels would depend more on the occurrence of smaller sulfide particles than the lower sulfur content in such steels. Also considered was the variation of the occurrence of EAC with cycling frequency and stress intensity factor range (ΔK). From the boundaries to the EAC regime, data are obtained that can be applied to the setting of upper bounding curves for the ASME Code.

KEY WORDS: environmentally assisted cracking, pressure vessel steels, sulfur, inclusions, modeling, fatigue (materials), cracking, environmental effects

The validation of light water reactor pressure vessel components makes use of defect assessment procedures contained in the ASME (American Society of Mechanical Engineers) Boiler and Pressure Vessel Code, Section XI, Appendix A. Contained within this section

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of the Code are reference curves in terms of crack growth rate (da/dN) expressed as a function of the applied stress intensity factor range (ΔK) . The present curves, introduced into the 1980 edition of the Code, contain curves pertinent to an air and a water environment, the latter being further subdivided depending on the load ratio (R) experienced by the component under consideration. The technical basis for the current reference curves is given in Ref 1.

Study of the factors that influence crack growth rates in low-alloy pressure vessel steels has been underway now for over 15 years. The detrimental influence of a water, as opposed to an air, environment was demonstrated first by Kondo [2] and Mager and Legge [3] and has been substantiated since by many investigators [4,5]. Progress with gaining an understanding of these factors has been aided to a great extent by the formation and subsequent expansion of the International Cyclic Crack Growth Rate Group (ICCGRG), founded in 1977. Within this Group, the Mechanisms subcommittee has discussed at length the interactions between the many variables that can affect growth rates, particularly those that affect the onset of EAC. As a result of experimental and theoretical studies by ICCGRG members and discussions within the Mechanisms subcommittee, attention has recently turned specifically to the role that sulfur-rich anions play in bringing about environmentally assisted cracking (EAC). In terms of plots of da/dN against ΔK , the occurrence of EAC results in a considerable increase in growth rates relative to non-EAC rates. This is illustrated diagramatically in Fig. 1.

A role for sulfur, present in wrought products principally as manganese-sulfide inclusions, had been strongly suspected for some years, first having been cited in Ref 6 by Bamford. Further interest was taken when it was demonstrated [7] that a dramatic increase in crack propagation rate was obtained by the addition of small quantities (1 ppm or so) of sulfate anions to the test environment. Additionally, fractographic work [8] indicated that manganese-sulfide inclusions dissolve in hot, pressurized water. It was also reported in Ref 8 that propagating fatigue cracks tended to grow "out of plane," seemingly in order to intersect (and subsequently dissolve) inclusions.

Corrosion fatigue tests carried out in a hot, pressurized water environment can be difficult and time-consuming in nature and therefore expensive to perform. This is particularly the case for certain conditions that are highly pertinent to reactor operation, for example, low cycling frequency tests at very high mean loads. Also, for essentially the same set of conditions, they suffer from poor repeatability with respect to the onset of EAC, if EAC occurs at all. Due to these problems, consideration was given to the formulation of a computer model of second-phase (sulfide) particle distributions and the manner in which they interact with a hypothetical crack front.

The Particle Influence Zone Model

The basic premise of the model is that sulfide particles, present in the steel, are made accessible to the water environment by the presence of a surface breaking crack. These sulfides, once exposed, are dissolved by the pressurized water environment, the product(s) of dissolution then bringing about EAC by their aggregated presence at the crack tip. There is no intention here of entering into the debate about the mechanism of EAC in this material/ environment system, whether slip dissolution or hydrogen embrittlement; the premise is that the presence of sulfur-containing anion(s) has a direct influence on the rate determining step for EAC. Similarly, there is no consideration in this model of the actual chemistry of



Applied stress intensity factor range ΔK (log scale) FIG. 1—Schematic representation of EAC and non-EAC fatigue crack growth.

the sulfur-containing anion(s) formed by the dissolution of the sulfide inclusions. In the text that follows, the word "sulfur" or "sulfide" will be used to describe the dissolution product(s) responsible for EAC, but this should not be taken as an assumption by the authors that the stable form of the sulfur species is sulfur.

The model, which we termed the Particle Influence Zone (PIZ) model, is set up to estimate the percentage of a line (crack front) that is under the influence of second-phase particles (sulfides). These particles are distributed throughout a matrix and, for those that the crack front has passed, that is, have been exposed to the water environment, dissolve at a predetermined rate. Before describing the manner in which the model runs, it is necessary to give a description of the data required for use in it: these include the following;

- (a) the volume percentage of second-phase particles,
- (b) the particle size and shape,
- (c) the particle influence zone, and
- (d) the dimensions of the matrix containing the particles.

Volume Percentage of Second-Phase Particles

In the model, the volume percentage rather than the weight percentage of second-phase particles is required. Estimates of volume percentage were made on the assumption that the sulfur present in the matrix is all in the form of a binary compound of manganese and sulfur (MnS), that the matrix was totally iron and that the density of the sulfide was half that of the matrix, this being taken as eight. This led to the estimate that the volume percentage of sulfide was approximately 4.43 times the weight percentage of sulfur present. In this respect, we have considered wrought products rather than weldments, but a similar form of calculation for copper sulfides, present in welds, yields a similar result.

Second-Phase Particle Size and Shape

A range of particle sizes was considered for use in the model. The size range was based on metallographic work [8] and information in Jernkontoret charts referenced in ASTM Practice for Determining the Inclusion Content of Steel (E 45-85). The particle shape was assumed to be spherical, primarily, in the first instance for ease of calculation. Other particle shapes are, of course, possible, for example, cylindrical, but are not considered here. Since the volume percentage, size, and shape of the particles are set, the total number of particles for any given volume of matrix is fixed. Within the matrix, the distribution of the particles is set randomly. The model can be run using a fixed diameter for all particles or with a range obtained by the use of a beta distribution [9], with fixed upper and lower limits on diameter. The absolute lower and upper limits of particle diameter were selected as 1 and 50 μ m, respectively. It was usual to select a more restricted range of particle sizes when running with a distributed particle diameter.

Particle Influence Zone

The term "particle influence zone" refers to the modeling of the dissolution of secondphase particles. In the following, this is described with reference to a single particle. The particle is thought of as consisting of a (large) number of subparticles; this figure was later considered to represent sulfur atoms and kept at a constant value. The value used was 2.74×10^{19} subparticles/mm³ of particle. The variables considered in this part of the model were as follows:

- (a) diameter of the particle,
- (b) crack opening displacement (COD) of the crack containing the particle,
- (c) rate of, and time for complete dissolution of the particle,
- (d) speed of subparticle motion away from the main particle,
- (e) rate at which subparticles are lost from the system, and
- (f) distances of the crack tip and mouth from the particle center.

In this part of the model, the particle is assumed to dissolve (c) at a rate proportional to its initial surface area (that is, diameter²). The assumption was made—using the information presented in Ref 8 for guidance—that a 30-µm-diameter particle would dissolve in 10 h; this enabled the constant term in this assumption to be estimated. On dissolution, the subparticles are assumed to expand into a volume that is a circular disk centered on the particle; the thickness of the disk is equal to the COD figure in (b). The location of the particle relative to the crack tip and also the crack mouth is considered. As the main particle dissolves, the number of subparticles within the disk is not symmetric, but is modeled such that more move towards the crack mouth than the crack tip. This bias, which is time independent, has been modeled using a decaying exponential. For particles at the crack mouth, only 5% of the subparticles go towards the crack tip; at a depth of 10 mm (from the crack mouth) 45% of the subparticles go towards the tip. The rate of increase (with respect to time) of the volume into which the subparticles spread (that is, dissolve) is taken as constant, with the assumption being made here that after a quarter of the time for the particle to dissolve totally has elapsed, half the number of subparticles present in the main particle have been dissolved. This assumption was used in preference to solution of the diffusion equation for the sake of ease of calculation. The equation used for this, plus subparticle loss from the system (discussed later), was:

$$n = \frac{3 \times N}{tpd} \times t - \frac{2 \times N}{tpd^{3/2}} \times t^{3/2} - pl \times t$$
(1)

where

n = number of subparticles dissolved,

N = total number of subparticles,

t = time (s),

tpd = time for particle to dissolve (s), and

pl = subparticle loss from system (number per second, no. s⁻¹).

The speed of subparticle motion away from the main particle (d) is the radial speed with which they leave the particle's surface. At the particle's surface, this, therefore, represents the rate of change of the influence radius. However, as the influence radius grows, the rate of growth decreases (although the subparticle speed remains the same) due to the assumption of a constant rate of increase in volume. The time taken to reach the COD distance is taken as negligible. This is similar to the spreading out of an oil droplet when placed on the surface of water. The rate at which subparticles are lost from the system (e) is self-explanatory and is taken as an overall net loss. This loss is time dependent and is additional to the loss that is connected with the proximity or otherwise of the particle to the crack mouth just discussed. This could represent the influence of an externally imposed flow, an electro-chemical potential gradient, or the adsorption of subparticles onto the crack faces as the particles dissolve.

When dissolving subparticles encounter the crack tip, that is, a barrier, the subparticles that would have occupied the volume "behind" the crack tip (that is, the volume forbidden to them) are assumed to redistribute themselves at the crack tip. This leads to a buildup in number of subparticles at the crack tip, their presence bringing about the possibility of EAC. It is this number and its dependence on the various input parameters that the model is set up to calculate. Note that each particle is assumed to influence the crack tip independently of any other particle, an assumption not strictly true for high sulfur contents.

Dimensions of the Matrix

There are three factors to be considered when deciding upon the extent of the matrix in which second-phase particles are distributed. These are the length of the crack front, the
"thickness" of the crack front, that is, the "crack front influence zone" and the crack depth.

The crack front length was chosen to be sufficiently large relative to the second-phase particle diameters to remove any possibility of statistical bias. In any given simulation, the length chosen was about 200 times the diameter of the largest particle. In order to reduce bias further, simulations were run a number of times (usually ten) using the same set of conditions.

The presence of the crack front influence zone variable in the model acknowledges the observation that crack fronts in corrosion fatigue specimens undergoing EAC tend to deviate "out of plane" to intersect inclusions [8]. In the model, the crack front is considered not as a line, but as a plane perpendicular to the direction of crack propagation. In this paper, the crack front influence zone was taken to be a variable, equal to the monotonic plane strain plastic zone size, and independent of particle size.

The crack depth is present as a variable since all particles that have been passed by the crack front could contribute to the subparticle density at the crack tip. The assumption is made that_x in order to reach its current position, the crack front has propagated through the matrix under conditions of a single cycling frequency and constant ΔK ; the equation used is due to Scott [10], for which $da/dN \sim \Delta K^3$. Depending upon the cycling frequency, not all of the particles necessarily contribute to the subparticle density at the crack tip since it is possible, in the model, for subparticles to be left behind by the advancing crack front.

Running the Model

The model is written in BASIC for running on a desktop computer. It is set up to present a picture of the concentration of subparticles along the crack front at any one instant; it does not provide information on concentration variations with time as the crack front propagates through the matrix. In order to avoid "edge effects," the variation in concentration only along the central 30% or so of the crack front is modeled. This variation can be presented either as the absolute number of subparticles present or the percentage of the crack front over which the concentration of subparticles exceeds some specified level (say, a "threshold" level).

The model runs by first establishing the dimensions of the matrix that is to be populated by second-phase particles. The in-plane dimensions of the crack are obtained in the manner just described, while the extent of the matrix perpendicular to the crack plane is the sum of the crack front influence zone and the diameter of the largest particle under consideration. From the selected volume percentage of second-phase particles and the dimensions of the matrix, the expected number of average-sized particles is calculated. The crack front is divided (along its length) into segments, the sizes of which are equal to the mean particle diameter. The matrix can now be considered as a series of "drawers," each one segment thick, into which particles are to be placed. The number of particles per drawer is selected using a Poisson distribution [11]; the size of each particle is chosen using the beta distribution described previously and the location of each particle within the drawer is chosen randomly (based on rectangular distributions). This method was considered preferable to selecting all three particle coordinates randomly. The manner in which the matrix is seeded is illustrated in Fig. 2.

The program now checks to see which of the particles present will contribute to the subparticle concentration at the crack tip. Particles whose surface do not lie within the crack front influence zone are assumed not to be intercepted by the crack and therefore do not contribute. Since the volume percentage of second-phase particles is low, the program does not check to see whether adjacent particles overlap. Similarly, it does not check to see if particles in neighboring drawers and similar distances back from the crack front are at



FIG. 2-Seeding of matrix by second-phase particles.

opposite extremes of the crack front influence zone. Given the low volume percentage of second-phase particles, this is unlikely to occur but, even if this did happen, work reported in Ref δ indicates that crack branching can occur such that both particles could be intercepted.

The model then calculates the extent to which each of the remaining particles has "dissolved" and the contribution that the subparticles from each make to the total number at the crack tip. From any one particle, the subparticles are considered to spread over the COD and length of the crack tip under the influence of that particle. This is illustrated in Fig. 3.



SUBPARTICLE DENSITY AT CRACK TIP





Among the investigations carried out using the PIZ model, the following will be described in detail:

- (a) effect of varying the volume percentage of sulfur while retaining the same particle size,
- (b) effect of varying the particle size while maintaining the volume percentage of sulfur constant, and
- (c) variation of subparticle number with varying ΔK level (at constant load ratio) and cycling frequency.

Results and Discussion

Figure 4 shows the effect of varying the sulfur volume percentage while keeping the particle size constant (at 20 μ m diameter). The effect of varying the particle diameter at constant volume percentage (0.02%) is shown in Fig. 5. In both these figures, other con-



ditions such as load ratio, rate of loss of subparticles, etc., were the same. From Figure 4, a tenfold increase in the volume percentage of sulfur results in approximately a tenfold increase in the number of subparticles at the crack tip. In Fig. 5, a tenfold increase in particle diameter leads to greater than a thousandfold increase in subparticle number at the crack tip. Taken together, these figures show that an increase in sulfide particle diameter has a far greater influence on subparticle number than an increase in sulfur volume percentage. Thus, considering a modern low-sulfur steel (approximately 0.005% by weight S, that is, 0.022% by volume S) and one produced, say, 20 years ago, with a higher sulfur level (up to approximately 0.025% by weight S, that is, 0.11% by volume S), the model indicates that, relatively speaking, the reduction in sulfur will have only a minimal influence on the propensity to EAC in these two materials. What is more important with regard to the relative ease with which EAC is seen in older steels, as opposed to modern ones, is the probable reduction in second-phase particle size in modern steels relative to older steels. In this respect, the model highlights the desirability for the size/shape control of sulfide particles rather than a reduction in sulfur content per se. This therefore suggests that the setting of a bounding curve in Section XI of the ASME Code for modern low sulfur steels may only be possible if one could be assured of a concomitant reduction in the size of second-phase sulfide particles.

Figure 6 shows the variation of subparticle number at the crack tip over a range of ΔK levels for a given cycling frequency. As ΔK increases, the number of subparticles present at the crack tip rises very rapidly (over a range of 1 MPa \sqrt{m}) to a peak; as ΔK increases further, the number reduces, but the rate of reduction is lower than the rate of rise of ΔK . Manipulation of the data used to plot Fig. 6 showed that the onset of the initial rapid increase in subparticle number is controlled by the rate of loss of subparticles from the system. The decrease beyond the peak is controlled (primarily) by the interplay of subparticle speed and the non-EAC growth rate as ΔK changes.

Choosing a pair of values for rate of subparticle loss and speed, and repeating the calculations for a range of cycling frequencies produces a surface representing the number of subparticles at the crack tip as a function of frequency and ΔK , see Fig. 7. If we now hypothesize that there is some critical threshold number of subparticles needed for the onset of EAC, then this figure reduces to a boundary on a frequency/ ΔK plot within which EAC would occur. Unfortunately, it has not been possible to establish this threshold number theoretically and so we were obliged to retreat to a phenomenological approach. We decided to make use of experimental corrosion fatigue data generated by ourselves and published by Tice et al. in Fig. 10 of Ref 12 for scaling purposes. This figure is reproduced here as Fig. 8. The single set of data at R = 0.7 and f = 0.1 Hz shown in this figure was used to fix the rate of subparticle loss and speed of subparticle motion. The threshold subparticle level was set at 10^{13} and the rate of subparticle loss and speed fixed at 5 \times 10⁷ s⁻¹ and 0.012 mms⁻¹, respectively. Other data required for input into the model (sulfur volume percentage, etc.) were, where known, pertinent to this test condition; otherwise, estimates were made. Thought was given to relating the threshold subparticle level (10^{13}) to a concentration (that is, ppm) value at the crack tip. However, this could not be done satisfactorily since it would have necessitated the introduction of some totally arbitrary dimension (a distance "back" from the crack tip) in order to create a volume into which the subparticles are dissolved.

Figure 9 shows a plot of cycling frequency versus ΔK for the conditions previously specified. Although based on estimates, it is interesting to consider further the shape of the boundary between the EAC and non-EAC regions. At low cycling frequencies, the lower threshold ΔK level for EAC follows our experimental data (taken from Fig. 8) reasonably well; at higher cycling frequencies, the experimental thresholds are at higher ΔK levels than predicted by the model. This may be explainable if the rate of subparticle loss were itself dependent



on cycling frequency, increasing as cycling frequency increases due to, possibly, stirring effects within the crack. Figure 9 indicates that the upper and lower threshold boundaries for EAC meet in the high frequency, low ΔK region, but do not at the low frequency, high ΔK end. The actual value of frequency and ΔK where the upper and lower boundaries meet is, for this set of conditions, of no practical significance. Thus, we would have to conclude that, with the inherent uncertainties associated with in-service conditions, there would be

is, for this set of conditions, of no practical significance. Thus, we would have to conclude that, with the inherent uncertainties associated with in-service conditions, there would be a constant danger of EAC with this material. However, reference to Figs. 4, 5, and 7 shows that, if the volume percentage of sulfur could be reduced, or, more significantly, the particle size reduced, then this "closing" frequency/ ΔK value would move to the right in Fig. 9. A



FIG. 7—Variation of subparticle number with cycling frequency, f, and ΔK .

point could be reached such that practical, in-service frequencies and ΔK values would be below this point and hence a steel produced to this standard would, according to this theory, be free from EAC in service.

The upper ΔK threshold in Fig. 9 represents the point at which EAC ceases by virtue of the ability of the crack front—growing at the non-EAC fatigue crack growth rate—to outpace subparticles as the ΔK level increases. This, therefore, should be equal to the "inert" environment growth rate used as an input into the model. Information from Fig. 9 can be used to calculate the slope of this inert environment growth rate line. Assuming that the growth rate per cycle follows the Paris-Erdogan type of law, then

$$C\Delta K^n \times \text{ cycling frequency}, f = \text{ a constant}, P$$
 (2)



FIG. 8—Effect of loading frequency on crack propagation rates in low flow PWR water at 288°C (from Fig. 10, Ref 12).



FIG. 9—Plot of cycling frequency versus ΔK .

which, on re-arrangement, gives

$$n \times \log_{10} \Delta K - \log_{10} Q = \log_{10}(1/f)$$
(3)

where Q = P/C.

A plot of $\log_{10}(1/f)$ versus $\log_{10}\Delta K$ is shown in Fig. 10. The slope of the line, which is the exponent of the inert environment $da/dN - \Delta K$ equation, is 2.68. This is lower than the



FIG. 10—Plot of log (1/f) versus log ΔK .

exponent of the Scott equation (that is, 3), but close to those derived by Eason et al. in their re-analysis of low-alloy steel/inert environment data (2.84 and 2.91) [13].

If the same procedure is applied to the lower threshold ΔK level, then one also obtains a straight line, the slope of which is 2.95; this plot is also shown in Fig. 10. Furthermore, if one makes use of the test data used previously (to fix the rate of subparticle loss, etc.), then the intercept of this line gives a value for the pre-exponential factor (C) in the Paris-Erdogan equation (of ~2.1 × 10⁻⁴ (mm/cycle)). This equation represents the locus of the "knees" of $da/dN - \Delta K$ curves (features illustrated in Fig. 1) for this particular steel undergoing EAC and sets an upper bound to possible growth rates.

Finally, it is considered worthwhile emphasizing the basic premise in this modeling work, namely, that EAC will occur provided that greater than some threshold number of subparticles are present at the crack tip. There has been no need to invoke any requirement for threshold levels of crack tip strain or strain rate, such has been done in other work in this field, for example, Ford [14]. This should not be taken as an assertion that such requirements or concepts are invalid, just that this model, based on a single requirement is able, reasonably well, to explain experimental observations of EAC without them. However, it is implicit in this model that cycling at some frequency is taking place and therefore the case of static loading is not addressed. The application of the model to this situation is among future developments being considered by the authors.

Conclusions

(a) The main conclusion to be drawn from application of this model is that the observation of EAC in low-alloy steels in a pressurized water reactor (PWR) environment can be explained by the sole requirement that greater than a threshold number of "sulfur" subparticles need to be present at the crack tip. There is no need to invoke any requirement of threshold levels of crack tip strain or strain rate, but this does not imply any inverse conclusion that such thresholds do not exist. (b) Based on this premise, the model shows that the occurrence of EAC in two steels of similar sulfur content would be more likely in the one containing the larger second-phase particles. If a threshold level of subparticles could be assessed, then a regime of second-phase particle sizes or sulfur contents or both could be derived for which EAC would not occur.

(c) For a given set of conditions, the range of cycling frequencies and ΔK levels over which EAC would be predicted by the model has been estimated. An illustration of how the boundary for the onset of EAC could be used to draw an upper bound crack growth rate curve was presented.

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Material Performance—II

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Effects of Stress and Stress History on the Magnitude of the Environmental Attack in Renè 80

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ABSTRACT: Sustained-load creep tests using smooth, round bar specimens of Renè 80 were conducted at 900°C (1652°F) in two environments, namely, laboratory air and a 90% Na₂SO₄/ 10% NaCl molten salt film. Results show approximately a factor-of-two reduction in the rupture life of specimens tested in the molten salt environment. Metallographic examination of the failed specimens showed greater depths of environmental attack in the cross section as stress level increased from 207 to 310 MPa (30 to 45 ksi). Below a "critical" stress level, the depth of environmental attack remains nearly constant. Failure initiated by cracking along oxidemetal interfaces resulting from oxygen penetration and the formation of internal oxide fingers in the substrate material. A periodic unloading/reloading fatigue cycle superimposed on sustained-load creep tests had no effect on rupture lives for specimens tested in laboratory air, and the depth of environmental attack remained constant. However, rupture lives obtained in the molten salt environment were significantly reduced by the periodic fatigue cycle where spallation of the surface oxide layer during cycling was extensive and the depths of hot corrosion attack were greater.

KEY WORDS: environmental effects, fatigue (materials), cracking, rupture life, oxidation, hot corrosion, superalloys, metallography

Two important criteria in the development of materials for gas turbine engine structural components are their elevated temperature mechanical properties and resistance to environmental degradation. As engine operating temperatures are pushed to higher limits in order to increase performance and fuel efficiency, environmental effects on the high-temperature, time-dependent material properties become increasingly important [1]. Of particular concern are high-temperature oxidation and hot corrosion of stressed components such as turbine blades. In the blade operating temperature range of 649 to 1038°C (1200 to 1900°F) environment has been shown to significantly affect creep and stress rupture properties [2–5]. In addition, properties such as low-cycle fatigue, high-cycle fatigue, and crack growth rates can also be affected by the type of environment [6,7].

In order to better understand the microstructure-property-environment interactions that occur in high-temperature service, laboratory tests must be representative of actual operating conditions. Experimental evidence indicates that unstressed oxidation and hot corrosion

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Ni	Cr	Со	Мо	Ti	Al	С	Other
Balance	14.8	9.8	3.8	5.4	3.2	0.17	7.4W

TABLE 1—Composition of Renè 80 (percent by weight).

tests may not be representative of the behavior of a material in actual service where stress and environment are expected to produce a synergistic effect [8-10]. Therefore, as a foundation for understanding how environment affects high-temperature material properties, this work investigates the influence of stress and stress history (cycling) on environmental degradation. Oxidation and hot corrosion under various combinations of sustained and cyclic loading were studied in order to determine the roles stress and stress history play in the high temperature environmental degradation of a representative gas turbine engine structural material.

Nickel-base superalloys are by far today's material of choice for high-temperature, highstress applications. In recent years, advances in processing metallurgy have produced superior polycrystalline materials, directionally-solidified alloys, and single crystals having excellent creep and rupture strengths, thermal fatigue resistance, and good oxidation and hot corrosion resistance. Alloy development continues at a vigorous pace to introduce new generations of superalloys to provide additional 10 to 40° C improvements in temperature capability [11]. As a result, the effects of higher temperature environmental attack are a prime consideration in this class of materials.

Material

The material used in this work is the nickel-base superalloy, Renè 80. Renè 80 is a cast, precipitation-hardenable alloy containing chromium and cobalt, with titanium and aluminum acting as the gamma-prime precipitation-hardening elements. Tungsten and molybdenum are added for solid-solution strengthening. Carbon is added to the alloy to form metallic carbides. These carbides promote excellent elevated-temperature creep resistance by forming a discontinuous chain along grain boundaries and hindering grain boundary motion. The composition is given in Table 1. The material was tested in the fully heat treated condition, as given in Table 2. The specimens used in this study were machined from cast rod stock. The specimens were threaded-end and had an overall length of 101.6 mm (4 in.), a gage length of 31.75 mm (1.25 in.), and a diameter of 6.35 mm (0.25 in.).

Experimental

Creep testing was performed using a sustained-load creep frame having a 9070 kg (20 000 lb) capacity and a 20-to-1 lever-arm ratio. The creep frame was equipped with a hydraulic ram mounted under the end of the lever-arm. The ram was actuated using computer control

TABLE 2—neat treatment for Kene 80.			
(a) 1204°C (2200°F)/2 h/Vac/FC (b) 1093°C (2000°F)/4 h/Vac/FC (c) 1052°C (1925°F)/4 h/Vac/FC (d) 843°C (1550°F)/16 h/Vac/AC			

TABLE 2—Heat treatment for Renè 80.

to provide unloading/reloading of the test specimen at a periodic interval. A load cell within the load train of the creep frame was used to provide closed-loop feedback control. Heating of the specimen was done using a clamshell-type resistance furnace. All tests were conducted at 900°C (1652°F).

The creep elongation was recorded using a specially designed extensometer consisting of two rods in two concentric tubes. The upper end of the extensometer assembly consisted of two knife-edges that were attached to the gage section of the specimen. The gage length was nominally 2.54 cm (1 in.). The extensometer tubes extended along the load train of the creep frame and down through the bottom of the closed furnace. The axial elongation was measured using a linear variable differential transducer (LVDT) located at the lower end of the rod-in-tube extensometer assembly outside the furnace. The extensometry was capable of resolving 2.54 μ m (0.0001 in.) displacement. The creep elongation was continually monitored through a microprocessor.

Tests were conducted in two environments, namely, laboratory air and a 90% Na₂SO₄/ 10% NaCl molten salt film. To prepare a specimen for testing (for both uncoated specimens and specimens to be salt coated), the gage section was polished with 600 grit silicon carbide paper. This was done to slightly roughen the ground surface finish from machining in order to allow a salt spray to coat the specimen uniformly. To apply the salt coating, specimens were thoroughly washed and rinsed after polishing with the silicon carbide paper, placed on a hot plate, and heated to 175°C. Specimen temperature was critical since if the specimen was too cold, the salt spray would not vaporize. If the specimen was too hot, vaporization occurred violently on contact, and spallation of the salt occurred. The salt spray was a saturated aqueous solution of 90% $Na_{3}SO_{4}/10\%$ NaCl by weight. The solution was sprayed on the heated specimen using a plastic non-aerosol trigger pump similar to those used on household cleaners. The pump nozzle was adjusted to give a fine spray, and the specimen gage section was coated with a very thin layer of dried salt. The layers of salt were overlayed to achieve a coating of approximately 7.0 mg/cm^2 of salt. Any salt deposited in the threads of the test specimen during spraying was washed away by immersing the threads in warm water.

Sustained-load creep tests were conducted at stress levels of 206.7 MPa (30 ksi), 241.2 MPa (35 ksi), 275.6 MPa (40 ksi), and 310.1 MPa (45 ksi). Tests were run until failure. Additional tests were interrupted prior to failure in order to compare damage after a fixed time interval. In addition, sustained-load creep tests with a periodic superimposed unloading/ reloading cycle were conducted at a stress level of 275.6 MPa. The time interval between these single fatigue cycles ranged from zero (pure fatigue with mean load) to 900 s. The fatigue cycle had a frequency of 0.25 Hz (4-s period). After testing, all specimens were sectioned just below the necked region of the failure. The cross-sections were mounted, polished, etched, and the environmental attack was examined using the scanning electron microscope (SEM) and X-ray energy spectroscopy (XES). Depth of the environmental attack was measured as shown in Fig. 1 using an optical microscope with a traveling stage. The amount of sound metal along each of twelve diameters, d_i , 15° apart in the cross section was measured. The average depth of penetration (DOP) was calculated as

$$DOP = \frac{1}{2} \left[d_0 - \frac{\sum_{i=1}^{12} d_i}{12} \right]$$
(1)

where d_i represents the individual measurements and d_0 is the initial specimen diameter.



FIG. 1—Metallographic technique for quantifying the depth of environmental attack.

Results and Discussion

Sustained-Load Creep

Figure 2 illustrates the typical creep behavior of Renè 80 in both environments: laboratory air and 90% $Na_2SO_4/10\%$ NaCl molten salt. Total strain in percent versus time is plotted, and the data show several key points. First, the rupture life is significantly reduced due to the presence of the molten salt. Second, the strain to failure is also reduced, indicating an embrittlement of the material. Third, the data show little effect of environment in the primary stage of creep. The creep behavior in both environments is virtually identical into the early region of secondary creep for approximately 20 h until the more aggressive environmental attack of the molten salt causes an earlier and more abrupt onset of tertiary creep. The



FIG. 2-Creep behavior of Renè 80 at 275.6 MPa and 900°C.

	E	nvironment	
Stress Level, MPa	Laboratory Air	90% Na ₂ SO ₄ /10% NaC	
206.7	978	459	
241.2	380	217	
275.6	239	77	
310.1	93	46	

TABLE 3—Stress rupture life of Renè 80 at 900°C, h.

creep data obtained in laboratory air show a much more gradual increase in creep rate as tertiary creep slowly begins to predominate in the latter portion of the test. Finally, although the secondary, steady-state stage of creep is not well defined at all test conditions, the minimum creep rate appears to be greater in the molten salt environment [12].

Table 3 lists the rupture life as a function of stress level in both environments. The molten salt environment results in approximately a factor-of-two reduction in the rupture life as compared to those obtained in laboratory air. Figure 3 shows rupture life plotted as a function of stress level on a log-log scale. The simple power law relationship

$$T_{\rm RUP} = A\sigma^{-p} \tag{2}$$

where A is a constant and p is the power law exponent, correlates the data quite satisfactorily. Table 4 gives the values of the constants, A and p, for both environments.

Depth of Environmental Attack

After creep testing, each of the failed specimens was subjected to a detailed metallographic examination. The photomicrograph in Fig. 4 shows a region of the specimen surface in cross



FIG. 3-Stress rupture life of Renè 80 at 900°C.

Environment	Α	р	
Laboratory air 90% Na ₂ SO ₄ /10% NaCl	$7.0831 \times 10^{15} \\ 1.9383 \times 10^{16}$	5.5542 5.8780	

TABLE 4—Constants in Eq 2 for power law creep at 900°C.

section showing the environmental attack typical for specimens tested in laboratory air. A very adherent, protective, chromium-rich oxide layer formed at the specimen surface. This relatively thin, non-porous oxide layer acts as a barrier to prevent further oxidation of the base metal after forming on the specimen surface. Note that only a small region of metal directly beneath the surface oxide layer has been depleted of alloying elements, particularly chromium, titanium, and aluminum. As a result, the gamma-prime Ni_3 (aluminum, titanium) precipitate phase has dissolved as shown in Fig. 4.

For comparison, the hot corrosion attack by the molten salt film is illustrated in the photomicrograph in Fig. 5. This photomicrograph shows a region of the specimen surface in cross section. Hot corrosion is the accelerated oxidation attack of a material that is coated by a thin film of molten salt in an oxidizing atmosphere. Sodium sulfate is considered to be the major corrosive constituent in hot corrosion attack [13]. Note that the outermost layer



FIG. 4—Typical oxidation attack of Renè 80 at 900°C.



FIG. 5-Typical hot corrosion attack of Renè 80 at 900°C.

of oxide is much thicker than that formed in laboratory air and that it penetrates into the alloy in a "finger-like" fashion. Figure 5 clearly shows that the extent of the alloy depleted zone and the depth of environmental attack are much greater for the specimens tested in the molten salt environment. Within the alloy depleted zone, small globular sulfide particles rich in chromium and titanium were found as a product of the hot corrosion attack. The surface oxide layer was found to be rich in chromium and contained significantly more titanium and aluminum than in the oxide layer formed during tests in laboratory air. The relatively thick surface oxide layer formed in the molten salt environment was very porous and non-adherent. In many cases, its exact thickness was difficult to determine since some of the oxide was often stripped away during metallographic preparation. The depth of environmental attack was relatively uniform around the circumference of the specimen and only a few instances of "spikes" caused by environmental attack down grain boundaries as reported by other investigators were observed in this study [2,3,9].

Figure 6 shows the DOP of the environmental attack by laboratory air as a function of time at various stress levels. The DOP values were obtained through metallographic analysis of specimens tested in sustained-load creep for fixed times shorter than the rupture life at the particular stress level. Of key importance is that the depth of environmental attack at any fixed time increases as the stress level increases. Environmental attack is significantly greater under an applied stress than in the unstressed condition. Note also that this effect



FIG. 6—Depth of environmental attack by oxidation at 900°C.

increases at longer exposure times. Figure 7 shows the DOP of the environmental attack by the molten salt film as a function of time at the same stress levels. Similar observations can be made for the hot corrosion attack as were made for the oxidation in laboratory air. However, it is clear that the effect of stress level on the magnitude of the environmental attack is more pronounced in the molten salt film and that the depths of environmental attack are greater in the molten salt environment than in laboratory air at any fixed exposure



FIG. 7—Depth of environmental attack by hot corrosion at 900°C.

	E	nvironment
Stress Level, MPa	Laboratory Air	90% Na ₂ SO ₄ /10% NaCl
0	5.19×10^{-12}	7.70×10^{-12}
206.7	3.69×10^{-11}	4.38×10^{-10}
241.2	2.08×10^{-10}	8.44×10^{-10}
275.6	4.27×10^{-10}	1.34×10^{-9}
310.1	6.93×10^{-10}	1.94×10^{-9}

TABLE 5—Parabolic rate constant for environmental attack at 900°C, cm^2/s .

time. Another feature that is evident in Figs. 6 and 7 is that the DOP at failure is nearly constant for each of the environments. For laboratory air, the DOP at rupture is approximately 150 μ m while for the molten salt film it is over 200 μ m.

The DOP data in both Figs. 6 and 7 can be adequately described using a simple parabolic relationship of the form

$$DOP = \sqrt{Dt} \tag{3}$$

where D is a parabolic rate constant and t is time. Table 5 gives the parabolic rate constants for each stress level in both environments. The parabolic rate constant can be viewed as a diffusion coefficient, and the values given in Table 5 are of the same order of magnitude as that reported for the diffusion of oxygen in solid nickel in an unstressed condition at 900°C [14]. Figure 8 shows the parabolic rate constant, D, as a function of stress level for both environments. Once again, this clearly shows that the DOP of environmental attack increases with increasing stress level. The molten salt environment results in much greater depths of attack when compared to those obtained in laboratory air. A third important point that is illustrated in Fig. 8 is the existence of a "critical" stress level below which the degree of



FIG. 8-Parabolic rate constant, D, for environmental attack at 900°C.

environmental attack remains essentially constant and at a magnitude close to that obtained in the unstressed condition [2].

Modeling the Creep Behavior

Research conducted in this laboratory and elsewhere has produced data that indicate that creep resistance under the influence of an environment is dependent upon specimen size [10, 15]. The explanation proposed is that only the undamaged cross section of the specimen contributes to the creep resistance. Therefore, a smaller diameter specimen would appear to have less creep resistance than a larger one if the depth of environmental attack were the same. This occurs because the fraction of "sound" material is smaller in the small specimen when tested under identical load and environmental conditions. To evaluate this hypothesis on the present data, a simple model for the rupture life was developed.

A simple linear summation model is proposed to predict the rupture life based on a fractional damage concept. The model is expressed as

$$\int_{0}^{t} \frac{dt}{T_{\text{RUP}}(\sigma, \text{ temp})} = 1$$
(4)

where dt is an increment of exposure time at a given stress level and temperature and T_{RUP} is the rupture life at this same stress level and temperature. Since the tests in this investigation were conducted at a single temperature, the model development is limited to the isothermal case. Noting from Fig. 3 that the data obtained under the two environments could be represented by the same form of equation (Eq 2), we postulate that the rupture life under an applied stress without any adverse environmental effect can also be represented as

$$T_{\rm RUP}(\sigma) = A\sigma^{-p} \tag{5}$$

The constants A and p are unknown. For the two cases where rupture life was determined in the presence of a degrading environment, the constants are those given in Table 4. Since the slopes of the two lines in Fig. 3 are nearly identical, that is, the constants, p, are nearly the same, we assume that the same constant, p, will be applicable in Eq 5 for the sound material with no environmental degradation. Note that the assumption of equivalent values for the constant, p, is questionable. The rupture life versus stress level curves (as in Fig. 3) for creep tests both in the absence and presence of an aggressive environment are expected to diverge (differing slopes) as stress level decreases. At the lower stresses (longer lives) where the environment has more time to act, the difference in the rupture lives of creep tests conducted in the absence and presence of an aggressive environment is expected to be greater than that at higher stresses (shorter lives) where environment should show a smaller effect,

Equations 4 and 5 can be applied to the cases where environmental attack has occurred by using the actual stress on the sound material in the computations. The stress is calculated from

$$\sigma = \frac{P}{\pi r_e^2} \tag{6}$$

where P is the applied load and r_e is the effective radius of the sound material. Denoting

as r the original radius of the specimen, Eq 6 becomes

$$\sigma = \frac{P}{\pi (r - \text{DOP})^2}$$
(7)

Introducing the expression for DOP in Eq 3, Eq 7 becomes

$$\sigma = \frac{P}{\pi (r - \sqrt{Dt})^2} \tag{8}$$

Note that the constant, D, is determined for each stress level in the experiments so that the equation is valid only for the particular nominal stress level in each experiment with the corresponding value of D. The environmental attack increases the stress level during the course of a creep test as given in Eq 8. An example of this increase in stress with time is presented in Fig. 9 for an initial stress level of 275.6 MPa. Note that the increase in stress is significant, particularly for the case of the test in molten salt.

The linear cumulative damage model, Eq 4, can now be written by combining Eqs 5 and 8 to obtain

$$\int_{0}^{T_{\rm RUP}} \frac{dt}{A \left[\frac{P}{\pi (r - \sqrt{Dt})^2} \right]^{-p}} = 1$$
⁽⁹⁾

The constant, p, is assumed to equal the value for laboratory air data given in Table 4 as p = 5.5542. The constant, A, can be determined by solving Eq 9 in an iterative fashion for a given stress level and experimental value of rupture life and the associated value of D. This was done for the case of the tests in laboratory air using the parabolic rate constants



FIG. 9—Increase in stress level due to the reduction in specimen cross section by environmental attack at 900°C.



FIG. 10—Linear cumulative damage model for rupture life of Renè 80 without environmental attack at 900°C.

from Table 5. The calculated values of A for the four stress levels were similar, so a single value was determined from the average as $A = 9.5434 \times 10^{15}$. These values for A and p determine the rupture life for a material that has undergone no environmental attack as calculated from Eq 9. The results are presented in Fig. 10 along with the results for the case of tests in laboratory air. It can be seen that there is a small effect on rupture life in the laboratory air environment due to the penetration and resultant reduction of cross-sectional area.

The same approach can be applied to the case of creep tests in a molten salt environment. In this case, however, we use the constants for the case of no environment to predict the rupture life in a molten salt film. The depth of penetration is calculated using the appropriate constants from Table 5. The predicted time to rupture is compared with the experimentally determined values in Fig. 11. It can be seen that the actual time to rupture is approximately half of that predicted from the model. This indicates that the reduction in cross-sectional area does not fully explain the behavior in a creep test in molten salt. One possible explanation is that the damage to the material from this hostile environment is beyond that of simply degrading the annulus identified by the depth of penetration. In that case, the integrity of the remaining sound material is less than that of the material tested in an inert environment, perhaps due to degradation along grain boundaries that is not seen using standard metallographic techniques. A second possible explanation is the non-uniformity of the DOP. In this case, the deepest penetration would be a better measure of damage (at the weakest or minimum cross section) than the average value used in the computations. Third, the assumption in the model that the value of the constant, p, is the same for the "inert" environment and the aggressive environment may be bad. The actual value of p needs to be experimentally determined by conducting creep tests in a vacuum or inert gas environment. In any case, the creep behavior based on the calculated sound material cross-sectional area has gone a long way in predicting rupture life of this material under aggressive environments.



FIG. 11—Linear cumulative damage model for rupture life of Renè 80 in molten salt environment at 900°C.

Creep with Cyclic Unloading

In order to assess the role of stress history on the magnitude of environmental attack, creep tests were conducted under sustained load with a superimposed periodic unloading/reloading fatigue cycle. In this type of creep/fatigue test, an increase in the number of fatigue cycles has been observed to cause an increase in crack growth rates in Inconel 718 [16]. In this study, it was postulated that such a periodic unloading/reloading fatigue cycle would cause mechanical damage to the surface oxide layer and result in greater depths of penetration. Figure 12 shows the waveform consisting of the sawtooth fatigue cycle and a



FIG. 12—Waveform of periodic fatigue cycle; $P_{min} = 0.15 P_{max}$.

	 E	ironment	
Hold Time, s	Laboratory Air	90% Na ₂ SO ₄ /10% NaCl	
0	294		
90	289	28	
900	281	37	
No cycling	239	77	

 TABLE 6—Stress rupture life of Renè 80 at 900°C and 275.6 MPa with superimposed periodic unloading cycle, h.

sustained-load hold time. Table 6 gives the rupture life as a function of the sustained-load hold time in both laboratory air and molten salt film. For the tests conducted in laboratory air, Table 6 shows that the superimposed fatigue had no effect on the rupture life under the test conditions used in this study. Post-failure examination of the specimens showed a continuous adherent surface oxide layer with no visible mechanical damage. As a result of this protective oxide layer, no increased environmental penetration occurred, and rupture life was not affected. Conversely, Table 6 clearly shows the reduction in rupture life due to the periodic unloading/reloading cycle for specimens tested in the molten salt film. Examination of the failed specimens after testing in the molten salt film showed extensive cracking and spallation on the specimen surface. The surface oxide layer was very fragile and non-adherent and crumbled even during careful removal of the specimen from the creep frame. This non-protective surface oxide layer resulted in greater depth of environmental attack and an associated reduction in rupture life. Figure 13 summarizes the effect of unloading/reloading on the depth of environmental attack. Note that the depth of penetration in laboratory air remained constant as the sustained-load hold time was reduced. However, in the molten salt environment, reducing the sustained-load hold time (increasing the number of fatigue cycles) caused an increase in the depth of penetration of the environmental attack.



FIG. 13—Effect of periodic fatigue cycle on the depth of environmental attack at 900°C.

It is interesting to also note that under sustained-load creep without a periodic fatigue cycle, the DOP in both environments is very similar at the time of failure.

Summary and Concluding Remarks

1. At a given stress level, the depth of environmental attack by the 90% Na₂SO₄/10% NaCl molten salt was significantly greater than the depth of environmental attack in laboratory air.

2. Approximately a factor-of-two reduction in the rupture lives of Renè 80 was observed for specimens tested in molten salt environment as compared to the lives obtained in laboratory air. The more aggressive environmental attack of the molten salt resulted in an earlier and more abrupt onset of tertiary creep and subsequent failure.

3. The depth of penetration (DOP) of environmental attack in both laboratory air and molten salt film is significantly greater under an applied stress than in the unstressed condition. Also, the DOP increased as the stress level increased from 207 to 310 MPa.

4. Below a "critical" stress level, the depth of environmental attack in both laboratory air and molten salt film remained nearly constant and at a magnitude close to that obtained in the unstressed condition.

5. Failure occurred in sustained-load creep initiated by cracking along oxide-metal interfaces resulting from oxygen penetration and the formation of internal oxide fingers in the substrate material.

6. The load-carrying capacity of the test specimens during creep was reduced due to a reduction in the amount of "sound" material in the cross-section by environmental attack. As a result, a significant increase of the stress level in the cross section occurred with time during the course of a test.

7. A linear cumulative damage model that accounts for the reduction in "sound" cross section due to environmental attack shows that this effect is in large part responsible for the decrease in rupture life in the molten salt environment as compared to results obtained in laboratory air. The model predicts rupture lives in the molten salt environment to within a factor of two of the experimental results.

8. In laboratory air, a periodic unloading/reloading cycle superimposed on the sustainedload creep had no effect on the depths of environmental attack or rupture life. The surface oxide layer remained adherent with no visible cracking. By contrast, in the molten salt film, rupture lives were significantly reduced due to the periodic fatigue cycle. In this case, spallation of the surface oxide layer was extensive and the depths of hot corrosion attack were greater than in the case without the periodic fatigue cycle.

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Role of Environment in Elevated Temperature Crack Growth Behavior of Renè N4 Single Crystal

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ABSTRACT: Sustained load creep and fatigue crack growth tests have been conducted over a temperature range of 870 to 1038°C for single-crystal (SC) Renè N4 nickel-base superalloy. Tests were conducted in both laboratory air and an inert environment of a vacuum of 10⁻⁵ torr under similar conditions to understand the role of environment in elevated temperature crack growth behavior of this material. Mini-compact tension type specimens were fabricated with orientation [001] parallel to the loading axis and [100] direction parallel to the crack growth direction. The creep crack growth rate in laboratory air at 870°C was found to be nearly an order of magnitude higher as compared to tests conducted in a vacuum of 10^{-5} torr. However, in fatigue at a stress ratio of 0.1 and a frequency of 1.0 Hz, the crack growth rate was found to be somewhat higher in vacuum as compared to growth rates obtained from tests in laboratory air. A number of constant K tests were conducted with different frequencies of 0.1 and 0.01 Hz and several hold-times to investigate the time-dependent effects. Fractographic studies of the fatigue crack growth specimens tested in laboratory air and vacuum did not show any distinct differences in failure mechanism. However, interdendritic failure was observed for creep specimens tested in laboratory air, while the fracture surface obtained from vacuum tests showed crystallographic features.

KEY WORDS: fatigue crack growth, creep crack growth, single crystal, environment, fractography, fracture mechanism, crystallographic fracture, fatigue (materials), cracking, environmental effects

The role of environment in the creep and fatigue behavior of nickel-base superalloys used in gas turbine engines has received a great deal of attention. A number of studies have shown that the environment can play a significant role in the fracture behavior of these alloys. In conventional polycrystalline materials, both creep and fatigue crack growth rates have been found to be affected by environment and are significantly greater in laboratory air as compared to that in inert environment [1-4]. Although the interaction of temperature, environment, and microstructure results in complex mechanisms, the general agreement has been that the increase in temperature enhances oxidation, and oxygen present in the laboratory air leads to the weakening of grain boundaries resulting in higher growth rates.

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However, for single-crystal materials, the absence of grain boundaries raises new questions regarding environmental effects at high temperature. The single crystals offer potential advantages in terms of their significantly improved creep rupture life and the elevated temperature fatigue strength over their conventionally cast polycrystalline or directionally solidified counterparts. However, their use at higher temperatures exposes them to accelerated kinetics of environmental interaction. This investigation is part of a continuing effort to understand the role of environment on the crack growth behavior of different classes of materials. This study specifically deals with the role laboratory air plays on creep and fatigue crack growth behavior of advanced Renè N4 single crystal. The main objective of this program is to understand the complex interaction of environment, microstructure, and temperature on the elevated-temperature crack growth behavior.

Experimental Procedures

Single-crystal Renè N4 casting slabs of 115 by 50 by 13 mm were obtained from a commercial vendor. The composition of this alloy in percent by weight is 9.25Cr, 7.7Co, 3.7Al, 4.0Ta, 4.2Ti, 6.0W, 1.5Mo, and 0.5Cb, with the balance nickel. The single-crystal slabs were solution treated at 1270°C for 2 h followed by aging at 1080°C for 4 h and 900°C for 16 h in inert environment. Mini-compact tension specimens of the dimensions shown in Fig. 1 were then machined out from the heat-treated slabs, such that the loading line axis of the specimen was oriented along [001] while the crack growth direction was along [100], later referred to as [001]/[100] orientation. Some of the specimens were side-grooved (25% on either side) to approximate plane strain conditions.

Crack growth tests were conducted both in laboratory air and vacuum. The creep tests were conducted on an Arcweld creep frame over a temperature range of 870 to 1038°C. The test procedure for creep crack growth tests in air and vacuum was similar to that described in an earlier paper [1]. The crack length data was reduced to the form da/dt versus K. The K was assumed to be a reasonable correlating parameter [5–7].

Fatigue tests were carried out in an automated servo-hydraulic testing machine under



FIG. 1—Side-grooved subcompact tension specimen (dimensions in millimetres).

computer control. Initially, constant load amplitude tests were conducted at 870°C both in air and vacuum at a frequency of 1.0 Hz and a stress ratio (R) of 0.1 to obtain crack growth behavior over a wide range of stress intensity. This was followed by a number of constant K tests conducted in air at frequencies of 0.1 and 0.01 Hz. Several other tests were conducted where the hold-time was varied from 10 to 500 s to investigate the time dependency.

The fatigue crack growth data were reduced to the form of crack growth rate per cycle (da/dN) versus stress intensity range (ΔK) using a modified incremental polynomial method [8]. To understand the mechanism of crack growth, a detailed fractographic analysis of all the fractured test specimens was conducted using a scanning electron microscope.

Results and Discussion

The creep crack growth behavior of single-crystal Renè N4 with [001]/[100] orientation in laboratory air at three different temperatures of 870, 925, and 1038°C is shown in Fig. 2. It is clear from these da/dt versus K plots that the creep crack growth rate increases with an increase in temperature. Such behavior is common with most materials and the higher



FIG. 2—Creep crack growth behavior of Renè N4 single crystal at 870, 925, and 1038°C.



FIG. 3—Surface features of sustained load specimen tested at 925°C.

creep crack growth rate at 925 or 1038 as compared to that at 870°C is thought to be due to faster kinetics of reactions at higher temperature. More tests in air are being conducted to establish the temperature dependence of creep in this alloy. One of the representative fractographs is shown in Fig. 3. Defects such as pores and inclusions appear to be more active at higher temperature in contributing to the crack growth as seen from Fig. 3. There is evidence of more secondary cracking, also.

Some selected tests were also conducted in vacuum. The creep crack growth behavior of single-crystal Renè N4 with [001]/[100] orientation in both laboratory air and vacuum at 870°C is shown in Fig. 4. It can be seen that the crack growth rate in air is nearly one order of magnitude higher than that in vacuum. There is also a distinct difference in apparent threshold stress intensity. One of the surprising features is that the difference between the air and vacuum curves is maintained even to high values of K where growth rates become significant. It thus appears that the role of environmental degradation into the material at the crack tip exceeds the crack velocity even at growth rates up to 7.5×10^{-8} m/s in air. Large differences in creep crack growth rates between air and vacuum have been reported for a number of conventional polycrystalline materials [1-4] and have been attributed mostly to the weakening of grain boundaries by oxide embrittlement. However, weakening sites such as grain boundaries are not available in single-crystal material. But, the existence of a dendritic structure as shown in Fig. 5 offers some possible explanation. The interdendritic regions on a fine scale are analogous, in some respect, with grain boundaries. These fine regions vary minutely in local chemistry as compared with the bulk region and are generally loaded with inclusions and inhomogeneties.

The fractured specimens from creep crack growth tests were analyzed under SEM to understand the differences in growth rate. Figure 6 is the fractograph taken from the creep crack growth specimen that was tested in air, which clearly shows an interdendritic failure. Here, the crack follows the interdendritic path, apparently weakened by oxygen diffusion that may embrittle the interdendritic constituents, some of which have higher affinity for



FIG. 4—Creep crack growth behaviors of Renè N4 single crystal tested at 870°C in laboratory air and vacuum.



FIG. 5—Solidification structure of single-crystal Renè N4 showing the primary dendrites.



FIG. 6—Surface feature of specimen tested under sustained load at 870°C in laboratory air.

oxygen. Further, the diffusion of oxygen is quite fast in this region as compared to the bulk material. Figure 7 shows the fracture surface of the creep crack growth specimen in the region where the transition occurs from stable crack growth (interdendritic) to fast fracture (crystallographic). The transition occurs at a growth rate that is above the maximum rate at which data were obtained, which is approximately 7.5×10^{-8} m/s. The crystallographic fracture mechanism, therefore, does not appear until growth rates above this value are obtained. This indicates that the environmental degradation into the material occurs at a


FIG. 7—Surface features showing the transition from interdendritic to crystallographic fracture.

rate that is in excess of this crack velocity. Up to this velocity, the growth rates in air and vacuum are significantly different due to the environmental effect and the resultant differences in fracture mechanisms. Only at very high crack velocities would the air and vacuum growth rates be expected to coincide when the velocity is faster than the rate of penetration of oxygen into the interdendritic region ahead of the crack tip.

For the case of specimens tested in vacuum, however, the crack front appears more crystallographic. In this case, the crack path is more homogeneous since there is little



FIG. 8—Surface feature of specimen tested under sustained load at 870°C in vacuum.

difference in the bulk and interdendritic region. There is no weakening of the interdendritic region in this case in the absence of oxygen. In vacuum, a higher stress intensity level is apparently needed to grow the crack, or a slower crack growth rate occurs at the same stress intensity level as compared to the air test. This is evidenced by the fracture surface in Fig. 8, showing a homogeneous and crystallographic feature with complete absence of interdendritic path.



FIG. 9—Fatigue crack growth behavior of Renè N4 single crystal at 870°C in laboratory air and vacuum.

The situation in fatigue, however, is not quite the same. Figure 9 shows the fatigue crack growth behavior at 870°C in laboratory air and vacuum. The crack growth rates in vacuum are slightly higher than those in air, contrary to our observation in creep. Similar differences in fatigue crack growth rates of single crystals have been reported by other investigators [9–12]. This test was conducted at a stress ratio of 0.1 where measurable closure levels were observed for tests conducted both in laboratory air and vacuum. These values are listed in Table 1. The closure contribution is accounted for in Fig. 10, where da/dN is plotted against $\Delta K_{\rm eff}$ where $\Delta K_{\rm eff} = K_{\rm max} - K_{\rm closure}$. The use of $\Delta K_{\rm eff}$ as a correlating parameter brings the crack growth behavior plots close to almost a single curve. This indicates that the difference



FIG. 10—The da/dN versus ΔK_{eff} plots of Renè N4 single crystal tested at 870°C in laboratory air and vacuum.

in crack growth rates in vacuum and laboratory air is mainly due to the increased closure in the air test contributed by oxidation. This results in a lower ΔK_{eff} in air than in vacuum. The small amount of closure in vacuum could be the result of surface asperities.

The lower crack growth rates observed in air at elevated temperature were attributed by Duquette et al. [12] to crack blunting mechanisms of Stage 11 fatigue crack growth at the surface, induced by bulk oxidation. In this investigation, the fracture surface of specimens tested in air and vacuum showed some differences in fracture features [13]. A higher contribution of Stage 11 was evident on the fracture surface obtained in vacuum, which caused some surface asperities leading to closure. This could be the reason for the small value of

Material	Environment	Temperature, °C	$K_{\rm clo}$, ^a MPa $\sqrt{\rm m}$	Mechanism	
Renè N4	air	870	8.0	non-crystallographic	
Renè N4	vacuum	870	4.4	non-crystallographic	

TABLE 1—Closure values obtained in laboratory air and vacuum.

^a $K_{\rm clo}$ was measured at crack arrest for air test and approximately 1×10^{-9} m/cycle for vacuum tests.

closure obtained in vacuum as shown in Table 1. This closure contribution, however, could not be used to rationalize the difference in crack growth rates. Hence, the lower crack growth rates in air most probably are caused mainly by oxide-induced closure.

The near plateau in crack growth behavior observed in air at intermediate levels of K, as seen in Fig. 10, is not well understood. However, it is felt to be the result of diffusion of oxygen into the substructure. It is postulated that the oxidation results in the embrittlement and degradation of microstructure of the specimen tested in air. This embrittlement and degradation of microstructural constituents leads to secondary cracking and branching resulting in lower overall crack growth rates in this region. At high K values, when the crack velocity is high, there is not enough time for the environment to degrade or embrittle the substructure, resulting in negligible secondary cracking. A considerable amount of secondary cracking was observed at intermediate levels of ΔK , for specimens tested in air, while no such cracking was observed at high ΔK values or on fracture surfaces of specimens tested in vacuum. At very low ΔK , the data from air and vacuum consolidate. In this region, very little secondary cracking was observed. It is speculated that the stress intensity is not adequate enough in this region to cause secondary cracking hence the da/dN versus ΔK plots merge together.

Tests conducted at different frequencies of 0.1 and 0.01 Hz do not show any distinct difference in growth rates as seen from Fig. 11, indicating little effect of frequency on growth rate. To emphasize the time-dependency aspect, several tests were also conducted with hold-times of 5, 10, 50, 250, and 500 s. The results are shown in Fig. 12. The addition of hold times of varying lengths does not appear to change the average growth rate, although it introduces a high degree of scatter. These results support the observations made from tests conducted at different frequencies, that the fatigue behavior is not time dependent. It appears that the oxidation in laboratory air occurs very quickly and the kinetics is fast enough to produce a reasonable size oxide layer on the fresh surface exposed even for tests at a frequency as high as 1.0 Hz. This oxide layer is suggested to contribute to closure at a stress ratio of 0.1. Thus, oxide-induced closure appears to be a rational explanation for the apparent difference in the fatigue crack growth rates obtained in laboratory air and vacuum.

It is well known that crack growth at elevated temperature is influenced by the interaction of stress, frequency, environment, and temperature, and that the mechanisms of creep crack growth (CCG) and fatigue crack growth are different. In these experiments, the stress intensity value in CCG tests was very high as compared to the tests conducted in fatigue. The interaction of high stress with environment may have a synergistic effect to cause increased environmental degradation leading to higher growth rates in laboratory air creep tests. In prior studies of stress-assisted environmental degradation of nickel-base superalloys [14], such accelerated damage was observed as a result of the interaction of high stress and environment. In this investigation, there appears to be a critical stress or stress intensity level below which such synergism is absent. Similar behavior has been observed by Richmond et al. [15]. Once the stress is decreased below the critical level, just the normal oxidation



FIG. 11—Fatigue crack growth behavior of Renè N4 single crystal at 870°C at frequencies of 1.0, 0.1, and 0.01 Hz.

takes place, the kinetics of which are not fast enough to cause embrittlement or accelerated cracking. This appears to be the case in fatigue, where the applied stress intensity is below this critical level. As a result, the aggressive environment does nothing more than oxidize the surface. This oxidation, however, is enough to induce closure. It appears that several competing mechanisms are at work. For example, in the case of fatigue, there is competition between closure and oxidation. In vacuum tests, the small value of closure is the result of surface asperities with negligible effect of oxidation. In laboratory air fatigue tests, the normal oxidation induces additional oxide-induced closure to cause the difference in growth rates between tests conducted in laboratory air and vacuum. However, the kinetics of this oxidation at 870°C is too rapid to show any time-dependent effect, even for maximum hold-time tests. In creep, the kinetics of environmental damage is postulated to be accentuated by high stress levels. There is no closure present here and the accelerated environmental damage in laboratory air tests leads to higher crack growth rates.



FIG. 12—Hold-time effect on fatigue crack growth behavior of Renè N4 at 870°C.

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Environmental and Microstructural Influence on Fatigue Propagation of Small Surface Cracks

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ABSTRACT: The propagation of small surface cracks has been studied on a high-strength aluminum alloy 7075 in peak aged (T651) and overaged (T7351) conditions. Tests were performed at a load ratio R = 0.1 and a frequency of 35 Hz in ambient air and in vacuum. Small crack growth was monitored by mean of replicas. The behavior of small cracks is compared to that of long and short through cracks and discussed on the basis of closure measurements performed on long cracks. A strong influence of environment on small crack growth has been shown which is similar to that observed for through cracks in the low rate range ($<10^{-8}$ m/ cycle). The lower resistance observed in air has been related to water vapor embrittlement as previously shown to be large on crystallographic Stage I propagation observed in vacuum on the 7075 T651, but weak on Stage II propagation observed on the 7075 T651 in air and on the 7075 T7351 in both environmental conditions.

KEY WORDS: fatigue (materials), cracking, environmental effects, aluminum alloys, fatigue crack propagation, surface cracks, microstructure

Some years ago, studies conducted on the influence of environment on fatigue crack growth had shown that the fatigue resistance of metal is generally lower in atmospheric environment than in vacuum [1,2]. More recently, studies have been carried out in the low rate range and near threshold condition on several high-strength aluminum alloys [3-17] and aluminum-lithium alloys [18-20].

In the last decade, short and small fatigue cracks (following the terminology suggested in Ref 21) have been widely studied [21,22] while they have been recognized as an important field of research since Pearson's 1975 observation [23] of an anomalous behavior relative to conventional long cracks. But few studies have been dedicated to the influence of environment on short and small cracks, specially on aluminum alloys. At first Lankford [24] has observed very low environmental influence on small surface cracks grown in a 7075 T651 alloy in ambient air and in purified nitrogen [2 ppm water (H₂O)]. More recently a comparative study of short and long through cracks grown in a 7075 alloy in T651 (Fig. 1) and T7351 conditions [25,26], has shown a large influence of environment on the propagation of short through cracks in air and in purified nitrogen ($p_{H_{2O}} \sim 0.3$ Pa), compared to vacuum ($p_{H_{2O}} < 5.10^{-4}$ Pa). This environmental influence has been shown comparable to that ob-

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FIG. 1—Short through crack data in air (\blacktriangle) and vacuum (\bigcirc) compared to long crack data in air (∇) and vacuum (\bigcirc) for 7075 T651 CT specimens tested at R = 0.1 and 35 Hz [25].

served on long cracks in the low rate range ($<10^{-8}$ m/cycle) and a rationalization of long and short through crack propagation in terms of the effective stress-intensity factor range ΔK_{eff} has been verified as observed elsewhere on other alloys [27–30]. But such rationalization cannot account for the environmental influence as shown in Fig. 2 for the 7075 T651.

The aim of this paper is to contribute to a better knowledge of the influence of ambient environment on the growth of small surface cracks on a 7075 alloy. Two aged conditions, peak aged (T651) and overaged (T7351), have been considered to get information on the role of microstructure.

Experimentals

The composition in percent by weight of the 7075 alloy was 6.0Zn, 2.44Mg, 1.52Cu, 0.20Cr, 0.16Fe, 0.07Si, 0.04Mn, 0.04Ti, aluminum (balance). The alloy was quenched after hot rolling, 2% stretched and then aged 24 h at 120°C (peak aged T651) or 6 h at 107°C + 24 h at 158°C (overaged T7351). The average grain size of the pancake structure is 40 by 150 by 600 μ m.

The microstructure consists of Güinier-Preston (GP) zones (~1 nm diameter) and ν' (Mg₄ Zn₁₁ Al) coherent plates (1.5 by 5 nm diameter) in the peak aged condition, and M (Mg Zn₂) and T' (Mg₃₂ (Al,Zn)₄₉) large semi-coherent precipitates (~20 nm diameter) in the overaged alloy.

The specimens used for long crack tests were of single edge notched (SEN) type machined so that the stress axis upon testing would be parallel to rolling direction. The specimen width was of 18 mm and the thickness of 6 mm.



FIG. 2—The da/dN versus ΔK_{eff} relationships for short through cracks in air (\blacktriangle) and vacuum (O) compared to the effective data for long cracks in air (\bigtriangledown) and vacuum (\bigcirc) corresponding to propagation data presented in Fig. 1 [25].

The specimen type for small surface cracks used in the same loading conditions, is presented in Fig. 3.

Tests were performed on an electrohydraulic machine in ambient moist air (relative humidity $\sim 50\%$) or in an environmental chamber providing vacuum better than 5.10^{-4} Pa.

Long crack threshold tests were performed using a shedding procedure in accordance to the ASTM Test Methods for Measurements of Fatigue Crack Growth Rates (E 647-86a) recommendation to minimize overload effects at growth rate $<10^{-8}$ m/cycle.

Data for both large and small cracks were characterized using standard Mode I stress intensities.

For long cracks the relation for specimen ends free to rotate is

$$\Delta K = \Delta \sigma \sqrt{\pi a} \left(1.12 - 0.23 \, a/w + 10.6(a/w)^2 - 21.7(a/w)^3 + 30.4(a/w)^4 \right)$$



FIG. 3—Geometry of specimens used for small surface crack tests (all dimensions in mm).

For half penny small surface cracks of length 2a, the expression used is

$$\Delta K = 1.32 \, \bigtriangleup \sigma \, \sqrt{a}$$

Tests were run at a stress ratio R of 0.1 and a frequency of 35 Hz.

Small cracks were nucleated by cycling at increasing load. Crack extension was measured at constant loading by replicating the specimen gage section periodically. Replicas were then inspected using optical or scanning microscope to determine the crack growth history.

Long cracks were optically monitored by means of a traveling microscope ($\times 200$).

Closure measurements for long cracks were performed using the compliance technique by means of a displacement gage mounted at the mouth of the notch. The crack opening displacement was recorded with respect to the load at a frequency of 0.2 Hz in accordance with the mechanical performance of the X-Y plotter used.

Experimental Results

Overaged Alloy (T7351)

In Fig. 4, the fatigue crack propagation rates in ambient air are plotted versus ΔK for a small surface crack and a long through crack. The da/dN versus ΔK_{eff} relationship obtained from closure measurements for the long crack, and short through crack data obtained on a SEN specimen reported previously in Ref 26, are plotted in the same figure.

The long crack data are in accordance with previous observations on the same alloy [3,13,14]. Closure measurements show a large decrease of ΔK_{eff} in the low rate range with an effective threshold range about 0.45 MPa \sqrt{m} .

Propagation of short and small cracks is very similar and appears independent of the length at the beginning of the measurements, respectively of 140 and 6 μ m.

It can be inferred from the da/dN versus ΔK_{eff} curve that propagation of the small surface crack began without any closure.



FIG. 4—The 7075 T7351 alloy tested in ambient air at R = 0.1 and 35 Hz. Small surface crack data (\blacksquare) compared to long crack data ($\textcircled{\bullet}$) and da/dN versus ΔK_{eff} data (\oiint) for long crack. Short through crack data ($\textcircled{\bullet}$) are taken from Ref 26.



FIG. 5—The 7075 T351 alloy tested in vacuum at $\mathbf{R} = 0.1$ and 35 Hz. Small surface crack data (\Box) compared to long crack data (\bullet) and da/dN versus ΔK_{eff} data for long crack (\bigcirc).

The stress level to initiate and propagate the surface crack was of 273 MPa, which was about 60% of the yield strength σ_y . The correction factor proposed by Chan [31] to take into account the influence of local plasticity, could lead to an increase of about 8% in the value of ΔK which can hardly change the da/dN curves considering the experimental scatter. These results suggest a low effect of plastic constraint and of microstructure.

The da/dN versus ΔK relationship for the long crack and the small surface crack grown in vacuum are plotted in Fig. 5 with the da/dN versus ΔK_{eff} relationship for long cracks.

Typically the propagation in vacuum is slower than in air for small as well as long cracks.

The threshold range ΔK_{th} and the effective threshold range $(\Delta K_{eff})_{th}$ for long cracks are respectively of about 3.2 and 2.0 MPa \sqrt{m} in vacuum compared to 2.2 and 0.45 MPa \sqrt{m} in air (Fig. 4). This suggests a higher closure effect in air than in vacuum and shows a large environmental effect that is consistent with previous observations on long crack propagation [14].

The growth of the small crack in vacuum was initiated at a high stress level of 423 MPa (95% of σ_y). The corresponding Chan correction of 58% would translate the first experimental point within the da/dN versus ΔK_{eff} curve. This would again suggest that small crack propagation begins without any closure and with low influence of microstructure, which is in accordance with further growth data without dip [24].

These results in vacuum are qualitatively in agreement with the observations made here above with respect to the crack propagation behavior in air.

Peak Aged Alloy (T651)

In Fig. 6, the fatigue propagation data in air of a small surface crack is compared to that of a long through crack. In the same figure short crack data obtained on a compact tension (CT) specimen [25] are taken from Fig. 1. The da/dN versus ΔK data obtained from closure measurements for the long crack and the envelope of the results obtained by Lankford [24] on the same alloy are also indicated in this figure.

As mentioned previously in the experimentals, the new data for long cracks presented in



FIG. 6—The 7075 T651 alloy tested in ambient air at $\mathbf{R} = 0.1$ and 35 Hz. Small surface crack data (\blacksquare) compared to long crack data (\bullet) and da/dN versus $\Delta \mathbf{K}_{eff}$ relation for the long crack ($\mathbf{\nabla}$). Short through crack data (\Box) are taken from Fig. 1 and Lankford results envelope (---) from Ref 24.

this paper were obtained on SEN specimens. The da/dN versus ΔK and da/dN versus ΔK_{eff} relationships are similar to that obtained on CT specimens on the same alloy (Fig. 1) in the growth rate range higher than 10^{-8} m/cycle; but in the low rate range, the crack growth is faster and ΔK_{th} is lower than on CT specimens. The da/dN versus ΔK_{eff} relation shows that crack closure cannot account for these differences. The $(\Delta K_{\text{eff}})_{\text{th}}$ value of 0.45 MPa \sqrt{m} is comparable to that obtained on the overaged alloy (Fig. 4), but is substantially lower than on the CT specimen (~0.9 MPa in Fig. 1).

The propagation of the small surface crack in air was obtained at a stress level of 294 MPa (0.56 σ_y) and the corresponding Chan correction factor is almost negligible with a value of 1.07. The length of the crack when it is detected was of 6 μ m, and the growth rate was very low, about 2.10⁻¹⁰ m/cycle. The corresponding point in Fig. 6 falls nearby the *da/dN* versus ΔK_{eff} curve that suggests a low influence of closure as observed on the 7075 T7351 alloy. Further crack growth shows a progressive increase of *da/dN* without any dip.

Lankford's experiments were performed at a substantially higher stress level (about 0.8 σ_y) corresponding to a correction factor of 1.25. With such a correction, the first measurements made by Lankford for just nucleated small cracks would also fall nearby the da/dN versus ΔK_{eff} relationship, but in a higher rate range. The observation of dips in the crack growth data by this author could be related to plastic constraint due to a higher stress level leading to a crack propagation regime corresponding to rates $>10^{-8}$ m/cycle and can be different from the one encountered here [14].

Comparison of small surface crack and short through crack data shows that, for crack lengths about 0.2 mm, a similar behavior is observed in both cases. In such conditions, the small surface crack interacts with about 2 grains in the transverse direction or 5 grains in the short direction while the short through cracks interacts with some 50 grains. So the observation of a similar behavior of both kinds of crack is consistent with a low microstructural influence on the growth of the small crack in air at moderate stress level.

Small surface crack and long crack data in vacuum are presented in Fig. 7. The da/dN versus ΔK_{eff} mean curve for long cracks, and the growth data of short through crack taken from Fig. 1 are also indicated in this figure.



FIG. 7—The 7075 T651 alloy tested in vacuum at $\mathbf{R} = 0.1$ and 35 Hz. Small surface crack data (\Box) compared to long crack data on SEN specimen (\bigcirc) and CT specimen (\bigcirc), and da/dN versus ΔK_{eff} mean curve ($-\cdot-$) for long and short through cracks. Short through crack data (\blacksquare) are taken from Fig. 1.

Results obtained for the long crack on the SEN specimen are comparable to that on the CT specimens [14].

The small crack was initiated at a stress level of 360 MPa (0.68 σ_y) corresponding to a correction factor for local plasticity of 1.13. Due to less frequent replications in vacuum, the crack was only detected at a length 2a of 29 μ m. In such condition, the length of the small surface crack and of the short through crack at the first measurement is comparable. Typically, the propagation of the small tridimensional crack is very much faster than that of the short bidimensional crack. It can be also noticed that the former was initiated at a very much lower ΔK range even after Chan's correction. Also it can be observed that the first experimental data for the small crack falls very far from the da/dN versus ΔK_{eff} curve determined for the long crack in this alloy (Fig. 7), which means that the behavior of the small crack cannot be rationalized in terms of ΔK_{eff} in the present case.

These results show a large microstructural influence on the growth of a small surface crack in the peak aged alloy in vacuum.

Discussion

Environmental Influence

The detrimental effect of ambient air on the fatigue crack propagation in aluminum alloys has been related to water vapor adsorption at the crack tip [11,32-34]. This phenomenon can reduce the material resistance to crack propagation by diminishing the energy U required to create a unit free surface of crack (Rhebinder effect [34]) as suggested [14] for propagation in the rate range higher than the critical rate for hydrogen embrittlement defined by Achter [35]. In such condition, the propagation can be described as in vacuum with a relationship derived from Weertman model [14,36]

$$da/dN = A \left(\Delta K_{\rm eff}\right)^4 / \mu \sigma^2 U \tag{1}$$

where

- A = a dimensionless constant,
- μ = elastic modulus, and
- σ = a flow stress that can be related to the cyclic yield stress [6].

At growth rates lower than this critical rate, a hydrogen embrittling mechanism is brought into action [14,25,36,38-40]; the corresponding environmentally assisted crack propagation is assumed to be governed by the crack tip opening displacement range Δ CTOD and can be described by the following relationship [14]

$$da/dN = B(\Delta K_{\rm eff})^2/\mu\sigma \tag{2}$$

where B is dimensionless.

Equation 2 is in good agreement with the da/dN versus ΔK_{eff} data in Figs. 4 and 6 for da/dN ranging from 2.10⁻¹⁰ m/cycle up to 10^{-8} m/cycle in air, and Eq 1 accounts for effective data in vacuum in a wide rate range for the 7075 T7351 (Fig. 5) while two different regimes have to be distinguished for the 7075 T651 (Figs. 2 and 7), the Regime I corresponding to a crystallographic mode of propagation [14].

On the basis of the foregoing considerations it can be inferred that the propagation of small surface cracks in air at rate ranging from 2.10^{-10} to 10^{-8} mm/cycle is environmentally assisted.

 $(\Delta K_{\text{eff}})_{\text{th}}$ in air in both aged conditions has been measured at 0.45 MPa \sqrt{m} . But, as shown in Fig. 2, $(\Delta K_{\text{eff}})_{\text{th}}$ determined on 7075 T651 CT specimens tested at R = 0.1 is much higher, about 0.9 MPa \sqrt{m} . However, previous tests carried out in the same conditions in nitrogen (3 ppm H₂O) at R = 0.1 and 0.5 and in ambient air at R = 0.5, have given a $(\Delta K_{\text{eff}})_{\text{th}}$ value about 0.5 MPa \sqrt{m} on several aluminum alloys [4,14]. This value, considered as a characteristic effective threshold range for aluminum alloys in wet environment, is consistent with the effective threshold range measured in the present study. Such difference in $(\Delta K_{\text{eff}})_{\text{th}}$ with specimen geometry can be related to previous observations.

On the first hand, near threshold crack surfaces of CT specimens of the 7075 T651 alloy tested in ambient air at R = 0.1 have been shown oxidized [7-13]. It has been suggested that oxide deposits can act as water trap and thus reduce drastically water vapor transport up to the crack tip. Such oxide production is assumed to be enhanced by Mode II crack opening [10,14,15].

On the second hand a study of the geometry effect has suggested that the propensity for Mode II opening is more pronounced for bending and CT specimens with respect to SEN specimens [41]. So, the higher ΔK_{th} and $(\Delta K_{eff})_{th}$ levels measured in air at R = 0.1 on CT specimens cannot be analyzed only in terms of mechanical closure effects, but could be related to a more extensive oxidation of the CT specimen surfaces and a subsequent inhibition of the influence of water vapor. Scanning observations on replicas of the crack surface, after removing the oxide layer, have shown at R = 0.1 a crystallographic growth path similar to the one in vacuum [13], which supports the above hypothesis for the peak aged alloy.

Influence of Microstructure

Comparison of Figs. 4 and 6 shows a substantial higher resistance to propagation in air of a small surface crack growing in the peak aged alloy. The difference in growth rate observed between the two aging conditions at the beginning of the propagation is large, but it is low when the crack is larger and the propagation similar to the one of a long crack at a rate about 10^{-8} m/cycle. On another hand, in the low rate range, the da/dN versus ΔK_{eff} relationships are identical for the two aged conditions. This indicates a larger closure influence on the peak aged alloy that can be related to roughness effect [13]. But in the mid rate range the da/dN versus ΔK_{eff} relationships are very different, which shows a lower resistance to crack propagation and suggests a higher sensitivity to water vapor of the peakaged alloy. Wei et al [42] have recently shown on a 7075 T651 alloy a corrosion effect of magnesium that could explain the stress corrosion susceptibility of the 7000 series alloys. Such corrosion effect could also give an explanation to the difference in the propagation behavior observed in air between the peak aged and the overaged 7075.

Comparison of small crack propagation in vacuum in the two aged conditions mainly show that nucleation is observed at about the same stress level (but at a different $\Delta\sigma/\sigma_y$ ratio). The propagation rates are comparable at the beginning of the growth, but further crack arrests are only observed on the peak aged alloy which indicates the presence of microstructural barriers.

Figures 8 and 9 show the microfractographic aspect of small surface cracks grown in vacuum within the site of nucleation at intermetallic precipitates in both alloys. A predominant Stage II crack growth mechanism can be observed in the underaged alloy while a Stage I regime is detected in the peak aged condition. Comparable behavior have been shown in the low rate range for long cracks [14]. Stage I crystallographic propagation near threshold in the 7075 T651 has been related to a localization of the plastic deformation at the crack tip to a single slip system in each individual grain. Such a localization can be related to the development of persistent slip bands (PSB) [43] in the peak aged matrix which contains coherent and shearable GP zones and ν' precipitates, while larger and less coherent precipitates favor dislocation by-passing and Stage II cracking in the overaged condition [14,44]. The same micromechanism appear to be involved in the small surface crack propagation. Crack arrests observed in the T651 condition can be related to a barrier effect of grain boundaries as described elsewhere [24,45] when single slip is operative.



FIG. 8—Fracture surface of a small surface crack nearby the nucleation site on the 7075 T7351 alloy tested in vacuum.



FIG. 9—Stage I propagation of a small surface crack nearby the nucleation site on the 7075 T651 alloy tested in vacuum.

The observations made on the alloy tested in air (Fig. 10a and b) suggests that environmental embrittlement induces Stage II propagation. A model used to account for hydrogen assisted cracking in aluminum-zinc-magnesium alloys [46] has been based on hydrogen enhanced localized plasticity resulting from the enhancement of dislocation motion and reduction of flow stress near the crack tip. The above observations made on the 7075 T651 alloy suggest that the enhancement of dislocation motion can result in the activation of several slip systems in the peak aged matrix promoting Stage II cracking in active environment instead of Stage I as in vacuum. The impossibility to rationalize in terms of ΔK_{eff} the behavior of small cracks on the peak aged alloy in vacuum, can be correlated to the existence of a Stage I propagation, in which case linear-elastic fracture mechanics (LEFM) fails to evaluate ΔK even after correction for local plasticity.

Conclusions

A strong influence of environment on propagation of small surface cracks has been shown on the 7075 alloy in two aged conditions, T651 and T7351; faster growth rate and lower resistance to crack nucleation have been observed in ambient air compared to vacuum.

The lower resistance to crack propagation in air has been related to water vapor embrittlement as previously shown for long cracks.

A large influence of microstructure has been shown on small crack growth in the peak aged alloy in vacuum, in which conditions Stage I propagation is observed. But a weak microstructural influence has been shown on Stage II propagation in the other experimental conditions (7075 T7351 in vacuum and in air, 7075 T651 in air).

The enhancement of the stress-intensity factor due to local plasticity can be taken into account by the model proposed by Chan [31] for Stage II small surface cracks.

As inferred from the effective data of long through cracks, the growth of Stage II small cracks might be rationalized with that of long and short through cracks in terms of the



FIG. 10—Fracture surface of a small surface crack nearby the nucleation site on the 7075 T7351 alloy (a) and on the 7075 T651 alloy (b) tested in air.

effective stress intensity factor range (including Chan correction). Such rationalization is not possible for Stage I cracks.

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Environmentally Induced Fatigue Crack Propagation Under Variations in the Loading Conditions

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ABSTRACT: In order to evaluate the influence of the environment on the crack retardation behavior under variable loading conditions, high-low block loading tests were performed in vacuum, air, and a 3.5% NaCl (sodium chloride) solution. In an additional test series, variations of the environment from vacuum in the high loading period to air or to 3.5% NaCl solution in the low loading period were performed, and vice versa. These tests, together with an extensive study of the crack surface morphology gave insight into the different fatigue mechanisms induced by the various environments at the crack tip.

A further test series was performed, where the load level was kept constant (constantamplitude loading) and only the test environment was changed. The results show a variation of the environment from the 3.5% NaCl solution to vacuum causes a retardation in fatigue crack propagation.

KEY WORDS: fatigue crack propagation, variable amplitude loading, environmental influence, aluminium alloys, fatigue delay, fatigue (materials), cracking, environmental effects

Important parameters controlling the fatigue crack propagation behavior are the mechanical properties, cyclic stresses and strains acting at the crack tip, the environmental conditions, and the microstructure of the material. A large amount of experimental and theoretical work has been performed to study environmentally induced fatigue crack propagation behavior under constant-amplitude loading. However, few systematic studies of the influence of the environment under variable-amplitude loading conditions have been performed [1-4].

Variations in the loading conditions from a higher to a lower load level or single-peak overloads cause a pronounced retardation in crack propagation. Tests in 3.5% NaCl (sodium chloride) solution with a single-peak overload showed that the number of delay cycles as well as the affected crack length (the crack length where retardation occurred) is significantly decreased from the results obtained in laboratory air [1]. The results of test series performed by Schulte et al. [2] in air and vacuum show that under a high-low block loading sequence the number of delay cycles and the affected crack length increases in vacuum.

Although it can be difficult to identify the actual contour of the plastic zones in front of

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Alloy	Cu	Zn	Mg	Mn	Cr	Si	Fe	Al
2024 X-7075	4.84 1.5	0.06 5.7	1.51 2.5	0.53	<0.001	0.15 0.003	0.35 <0.003	base base

TABLE 1—Chemical composition of the alloys investigated, percent by weight.

the crack tip of fatigue loaded materials, some correlation between the affected crack length and the plastic zone size has been reported. This suggested [3,5,6] that differences in the plastic zone size in vacuum and in air are the reason for the different affected crack lengths measured after a single-peak overload.

Analyses using continuum mechanics assume that the size of the plastic zone is dependent on the magnitude of the applied load, on the yield strength, and on the plastic strain hardening behavior of a material. Furthermore, various models that predict the fatigue crack propagation under variable-amplitude loading are based on changes in the plastic zone size at the crack tip. If an aggressive environment increases the constant-amplitude fatigue crack growth behavior by decreasing the plastic zone size and consequently the affected crack length, it is necessary to consider these effects in the prediction models.

Experimental

In order to gain a deeper insight into the environmental effects on the fatigue crack growth behavior under variable-amplitude loading, a test program was performed where both the alloys and the environment were varied. The commercial aluminium alloy, 2024-T3, and the laboratory alloy, X-7075, were tested in an inert environment (vacuum), laboratory air, and in a 3.5% NaCl solution. The 2024-T3 was used in the as-received condition. The laboratory alloy, X-7075, is a high purity derivation of the commercial Al-7075 containing no chromium, silicon, and iron [7] and was used in the underaged condition after a final heat treatment of 24 h at 100°C. The chemical composition of the alloys is shown in Table 1. The resulting tensile properties of the two alloys are given in Table 2 (where E = elastic modulus, $\sigma_{0,2} =$ yield stress, $\sigma_B =$ ultimate tensile stress, and $\epsilon_B =$ true fracture strain).

Constant-amplitude (CAL) and high-low block loading tests were performed to evaluate the environmental influence on the crack retardation behavior. Further tests were performed changing the environment from vacuum in the high loading period to air or the 3.5% NaCl solution in the low loading period, or vice versa. An additional test series was performed with CAL and variations in the test environment.

For the fatigue crack growth tests, center cracked specimens (230 mm long, 80 mm wide, and 1 mm thick) were used. The tests with constant-amplitude loading and with high-low loading sequences were performed with a stress ratio of R = 0 in the constant-amplitude loading tests and in the low loading level of the high-low block loading sequence, and with R = 0.33 in the high loading level of the high-low block loading sequence. The variation

Alloy	Heat Treatment	E, MNm ⁻²	$\sigma_{0,2}$ MNm ⁻²	σ_B , MNm ⁻²	ε _B
2024	T3	74 000	340	716	0.4
X-7075	24 h, 100°C	72 000	423	730	0.33

TABLE 2—Tensile properties of the alloys investigated.

in the loading level occurred at crack lengths of 3 mm and 12 mm, which corresponds to ΔK -values of 9.73 MN m^{-3/2} and 20.37 MN m^{-3/2}. The test frequency was 20 Hz. The tests were performed at room temperature, in vacuum (10⁻⁴ Pa), laboratory air, and 3.5% NaCl solution. In order to avoid local pitting on the specimen and fracture surfaces, an inhibitor of 0.3% Na₂Cr₂O₇ + 0.2% Na₂CrO₄ was added to the NaCl solution.

To investigate the failure mechanisms, fractographic analyses were made with the scanning electron microscope (SEM).

Test Results

Fatigue Crack Propagation Under Constant-Amplitude Loading

The fatigue crack propagation behavior of X-7075 in the underaged condition is shown in Fig. 1a. It can be seen that the lowest crack propagation rates over the entire ΔK range occur in vacuum, while the fatigue crack propagation properties are the worst in the 3.5% NaCl solution. At low ΔK -values, the fatigue crack propagation rates in air are slightly smaller than in the NaCl solution. However, at high ΔK -values, the crack propagation curves approach the vacuum curves. For X-7075, laboratory air acts as an aggressive environment with the greatest influence at low ΔK -values. This is because at low ΔK -values the time available for the environment to influence da/dN is the longest. Figure 1b shows the fatigue crack propagation behavior of Al 2024-T3. For this alloy, the best fatigue crack propagation properties are also found in vacuum and the worst in the NaCl solution.

The differences in the fatigue crack propagation behavior of the different environments in both alloys become most pronounced at low da/dN values. But at high ΔK -values, the differences in the fatigue crack propagation behavior become less or even diminish.

Fatigue Crack Propagation Under a High-Low Block Loading Sequence

The test results are summarized in Table 3 where N_D and a^* refer to the number of cycles and the range in crack lengths, respectively, over which retardation has occurred. Figure 2 schematically shows how the number of delay cycles and the affected crack length were calculated. In Fig. 3a, the observed crack propagation behavior of X-7075 during a highlow loading sequence is shown for the three environments investigated. The curves all show the same general trend: the crack propagation rates decrease considerably after the drop in the loading level. However, the minimum in the crack propagation rates is most pronounced for the test performed in vacuum. The lowest retardation is observed in the tests made in the NaCl solution.

The affected crack length, a^* , is influenced by the environment. It is the smallest in the NaCl solution and the largest in vacuum for both alloys investigated. When a variation in load is performed at the short crack length of 3 mm (that is, low da/dN rates) almost no retardation can be observed in the NaCl solution for X-7075 (Table 3a). Figure 3b shows the retardation behavior of 2024-T3. The fatigue crack propagation behavior shows the same general trend. However, the amount of retardation is larger in 2024-T3 for all environments (Table 3b). The results of Fig. 3b are also given in the form of an a versus N plot in Fig. 4a.

In Fig. 4b test results are shown for the case, where in addition to changes in the load level, the environment was also changed. The crack propagated at the high loading level in vacuum, and at the low loading level in air or in the 3.5% NaCl solution. The case where no change in the environment was performed is also shown. A comparison of the test results with those in Fig. 4a show that a vacuum environment in the high loading period leads to



FIG. 1—(a) Crack propagation behavior of Al X-7075, 24 h at 100° C, (underaged) in vacuum, air and in the 3.5% NaCl solution. (b) Crack propagation behavior of Al 2024-T3 in vacuum, air, and in the 3.5% NaCl solution.

	3 mm C	rack Length	12 mm Crack Length	
	a*		a*	N _D
(A) AL-X-7075 2	4 н, 100°с, тезтер	IN VACUUM, AIR AND	a 3.5% nacl solu	JTION
	(CONSTANT EN	VIRONMENT IN EACH TH	EST)	
Vacuum	850	515 000	5 000	111 600
Air	1 600	21 000	1 400	35 000
3.5% NaCl Solution	100	1 800	700	8 100
(b) al 202	24-t3, tested in VA	CUUM, AIR AND A 3.5	% NACL SOLUTION	
	(CONSTANT EN	VIRONMENT IN EACH TH	EST)	
Vacuum	3 000	1 250 000	5 600	1 080 000
Air	1 300	53 000	3 000	120 000
3.5% NaCl solution	470	24 000	2 000	36 000
(C) AL 20	24-t3, variation i	N THE ENVIRONMENT I	URING THE TESTS	
NaCl/vacuum	arrest	1 500 000	arrest	1 500 000
Vacuum/vacuum	3 000	1 250 000	5 600	1 080 000
Air/vacuum	1 300	338 000	2 600	271 000
Vacuum/air	1 200	125 000	2 200	244 000
Air/air	1 300	53 000	3 000	120 000
Vacuum/NaCl	150	3 000	2 600	46 000
NaCl/NaCl	470	24 000	2 000	36 000

TABLE 3—Crack growth retardation after a high-low loading sequence in terms of N_D (number of cycles with retardation) and a^{*a} (crack length with retardation), compare Fig. 2.

^{*a*} a^* measured in μ m.



FIG. 2—Crack growth retardation after a high-low loading sequence. Definitions of $N_{\rm D}$ and $a^*.$



FIG. 3—(a) Crack propagation behavior of Al X-7075, 24 h at 100°C, in vacuum, air, and in the 3.5% NaCl solution under a variation in the loading condition (high-low loading sequence). (b) Crack propagation behavior of Al 2024-T3 in vacuum, air, and in the 3.5% NaCl solution under a high-low loading sequence.

a higher retardation but to no significant change in a^* (compare Table 3c). Figure 4c shows the results of tests, where either air or a 3.5% NaCl solution was present in the high loading period and a change to vacuum at the low loading level was performed. The change from air to vacuum leads to a smaller retardation than in the case where only a vacuum environment was present at all load levels. However, in the case where the high loading period occurred in the 3.5% NaCl solution and the environment changed to vacuum in the low loading period, a complete arrest of the crack propagation over more than 1.5 million cycles was observed.

Finally, in an additional CAL test, where a change of the environment from the 3.5% NaCl solution to vacuum was performed at a crack length of 3 mm, a retardation in crack propagation after the change in the environment was also observed (Fig. 5).

Fractography

Figure 6 shows SEM photomicrographs of the fracture surface of X-7075 under constantamplitude loading conditions in the three different environments. This type of alloy exhibits a slip band type of crack propagation mechanism over the entire crack length in vacuum as well as in air (Figs. 6a-c). In vacuum, at low ΔK -values, the crack propagates transgranularly along intense slip bands (Fig. 6a), while at high ΔK -values, the fracture surface appears smoother, indicating that more slip systems are activated during the crack growth (Fig. 6b).



In air, even at low ΔK -values, many slip systems become active, leading to the flat appearance of the fracture surface (Fig. 6c). However, in a 3.5% NaCl solution, the crack propagates intergranularly at low ΔK -values (Fig. 6d).

For the commercial alloy, 2024-T3, no significant differences in the fatigue crack propagation mechanisms under constant-amplitude loading conditions could be observed in the three environments. The cracks propagated along slip bands at low ΔK -values (Fig. 7a) and, with increasing ΔK , a change to a crack propagation by void coalescence was observed (Fig. 7b).

Figure 8a shows the fracture surface of X-7075 after a high-low loading sequence in air. Fatigue striations that were formed during the high loading period can be identified. They cannot further be identified after the change to the low loading period. Figure 8b shows that a high-low loading sequence in a 3.5% NaCl solution leads to a change in the crack propagation mechanism, from a slip band type mechanism in the high loading period to a crack propagation along grain boundaries in the low loading period. This mechanism is observed as long as the crack is propagating in the retarded crack range.

The 2024-T3 shows at the 12-mm crack length, together with the change in the load level, a change in the fatigue crack propagation mechanism from a crack propagation by void coalescence in the high loading period to a crack propagation along slip bands in the low loading period (Fig. 9). This mechanism is most pronounced in vacuum, however, it can be observed in all three environments.



- (a) Crack retardation behavior in vacuum, air, and 3.5% NaCl solution (constant environment in the tests).
- (b) Crack retardation behavior in vacuum, air, and 3.5% NaCl-solution. Change of the environment from vacuum in the high loading level to vacuum, air, and 3.5% NaCl solution in the low loading period.
- (c) Crack retardation behavior in vacuum after a parallel change in the loading level (high-low sequence) and in the environment from vacuum, air, and 3.5% NaCl solution (at the high loading level) to vacuum

FIG. 4—Crack retardation behavior of Al 2024-T3 under a high-low loading sequence.



FIG. 5—Crack propagation behavior of Al 2024-T3 under constant-amplitude loading, with a change in the testing environment.

If the load level and also the environment are changed from vacuum to the 3.5% NaCl solution at the crack length of 3 mm, no distinct change in the crack propagation mechanisms occurred (Fig. 10*a*). However, at the 12-mm crack length, the fatigue crack propagation mechanisms clearly changed (Fig. 10*b*) from a crack propagation by void coalescence in the high loading period to an extremely slip plane orientated mechanism in the low loading period. This slip plane orientated mechanism can be observed over a crack length of about 700 μ m (Fig. 10*c*). Within this range, flat areas with irregular secondary cracks are formed (Fig. 10*d*) and debris being corrosion products can be identified.

Figure 11 shows the fracture surfaces for the case, where the environment has changed from air to vacuum with a parallel load variation. A change in the fatigue crack propagation mechanism is observed. At the high loading level, the formation of dimples (Fig. 11*a*) is seen as well as defined striations (Fig. 11*b*). The change in the environment and in the loading level abruptly stops the formation of striations, while some amount of crack propagation occurs by void coalescence. After some additional crack growth, the slip band-type mechanism dominates.

Figure 12 shows the fracture surface of the specimen that was fatigued in the 3.5% NaCl solution during the high loading period, and in the low loading period, it was exposed to a vacuum environment. In this case, no crack propagation was observed during 1.5 million cycles. After this observation period, the specimen was cracked in vacuum by tension. The fracture surface did not show any sign of a fatigue crack propagation in the vacuum environment.



NP/DP



FIG. 6-Scanning electron micrograph of the fracture surfaces of AI X-7075, 24 h at 100°C, specimens, fatigued in different environments.

N











(a) Air, crack length, 12 mm(b) 3.5% NaCl solution, crack length, 12 mm

FIG. 8—Scanning electron micrograph of the fracture surface of Al X-7075, 24 h at 100°C, specimens under a high-low loading sequence.



FIG. 9—Scanning electron micrograph of the fracture surface of Al 2024-T3 specimens under a highlow loading sequence in vacuum (crack length, 12 mm).

ronment. There were also some indications that the crack left material bridges near the crack tip voids during its propagation in the 3.5% NaCl solution.

Discussion

Fatigue Crack Propagation After a High-Low Loading Sequence Without a Variation of the Environment

The fatigue crack growth rates under CAL are strongly influenced by the environment. Under a high-low loading sequence (Figs. 3a and b and Tables 3a and b), the number of delay cycles, N_D , decreases the more aggressive the environment is. The overall retardation behavior in crack propagation after a high-low loading sequence has been described elsewhere [8]. However, the influence of the environment has not yet been satisfactorily discussed.

From the results shown in Figs. 1a and b, the following simple explanation may be derived: the differences in the number of delay cycles after the high-low loading sequences in the various environments are mainly due to the fact that constant-amplitude crack growth rates in air and in the 3.5% NaCl solution are higher than compared to vacuum at the same ΔK values. These differences in the constant-amplitude fatigue crack propagation are more pronounced at the low $da/dN \Delta K$ -values, which are present after the high-low loading conditions. For example, it takes fewer cycles for a crack to grow over a certain distance, that is, through the high load plastic zone in salt water, than in air and vacuum.

This is a very simple explanation, because it does not consider that retardation is the result of the interaction of several different processes acting together simultaneously. For example, the explanation does not consider the different crack propagation mechanisms in the various environments.

For a better understanding of the processes under variable loading conditions, the fatigue crack propagation behavior under constant-amplitude loading will be considered first in more detail. The constant-amplitude fatigue crack propagation behavior has extensively been investigated in Refs 7, 9, and 10. In these papers, hydrogen embrittlement has been proposed as the main factor for the environmental influence on fatigue crack propagation. Hydrogen embrittlement processes can only take place if hydrogen is adsorbed on the metal surface. Various adsorption, dissolution, and recombination processes are taking place simultaneously [10]. Transport of hydrogen into the bulk material must take place around the crack tip. This can occur by either diffusion or by a transportation mechanism due to dislocation movement [11]. However, it seems difficult to explain the embrittlement process merely by lattice diffusion during crack propagation, because the diffusion constant for hydrogen in aluminium is very low [12]. Albrecht et al. [13] have shown that in high-strength aluminium alloys dislocation transport of hydrogen is the main mechanism, and "it is kinetically preferred to volume diffusion because of the low diffusion constant of hydrogen in aluminum." Hwang and Bernstein [14] demonstrated the hydrogen transport mechanism through the movement of mobile dislocations. Therefore, transport of hydrogen by dislocation movement becomes more important for the explanation of the different crack propagation mechanisms observed in the three environments.

A transgranular crack propagation mechanism along intense slip bands was observed (Figs. 6a and 7a) and is due to the absence of hydrogen during fatigue crack propagation in vacuum at low ΔK -values. The concentration of the crack advance on only a few slip planes is caused by the fact that piled-up dislocations formed in the loading part can partly move back during the unloading part, which reduces the total crack advance in each load cycle [15].

The presence of a few slip systems also influences the crack tip morphology. Bowles [16] showed that the crack propagation in vacuum occurs microscopically at angles that differ from the macroscopic crack propagation direction and that branching occurs at the crack tip. The microscopical orientation, the branching of the crack tip, and the morphology of the crack front is rather irregular, leading to a stress state at the crack tip that deviates considerably from a Mode I situation. This results in a reduction of the effective stress intensity acting at the crack tip [17, 18].

A rough fracture surface causes early contact of the mating fracture surfaces during unloading in a load cycle. It has been shown previously that a greater roughness of the fracture surface has a strong influence on the crack opening stress level in an alloy and the retardation behavior after a high-low loading sequence [19]. This is corroborated by work done by Suresh et al. [20,21]. The reversibility of dislocation movement, the microscopical crack orientation, the irregular crack front, the micro-roughness of the fracture surface and the branching of the crack tip may be the main cause for the reduction in fatigue crack propagation in vacuum. It can also be expected that these phenomena are a main cause for the pronounced retardation in a high-low loading sequence in vacuum, as well.

In an aggressive environment, the crack propagation behavior is strongly influenced by hydrogen embrittlement. Hydrogen atoms that are produced at the bare metal surface at the crack tip can be transported into the bulk material by mobile dislocations [11, 13, 14]. The reversibility of slip and also the fracture stress are reduced. The crack mainly propagates by tensile decohesion [22]. Because of the different crack propagation mechanisms, as compared to vacuum, the crack tip morphology is also influenced. This becomes clearly visible by a comparison of Figs. 6a and c. Additionally, in the aggressive environment, the crack tip is more rounded [16]. The fracture surface is macroscopically more flat [22] and there is only a little effect on the magnitude of the effective stress intensity due to surface roughness. The described influences may be the main reasons for the higher crack propa-


FIG. 10—Scanning electron micrograph of the fracture surface of Al 2024-T3 specimens under a high-low loading sequence and with a change in the environment from vacuum to 3.5% NaCl solution.



FIG. 10-Continued.

(c) Crack length, 12.75 mm, 3.5% NaCl solution (d) Crack length, 12.05 mm, 3.5% NaCl solution



FIG. 11—Scanning electron micrograph of the fracture surface of Al 2024-T3 specimens under a high-low loading sequence. Alloy with change in the environment from air to vacuum.



FIG. 12—Scanning electron micrograph of the fracture surface of fatigued AI 2024-T3 specimens under a high-low loading sequence. Alloy with change in the environment from 3.5% NaCl solution to vacuum (crack length, 3 mm).

gation rates in an aggressive environment under constant-amplitude loading and for the reduction in retardation after a high-low loading sequence.

After the drop in the loading level during a high-low loading sequence, a change in the crack propagation mechanism was observed (Figs. 8 and 9). For the commercial aluminium alloy 2024, the mechanism changed from crack propagation by void coalescence in the high loading period to a propagation along slip bands in the low loading period. For alloy X-7075, the crack propagation mechanism changed from a slip-band-type mechanism in the high loading period to a fatigue crack propagation along grain boundaries in the low loading period, when the test was performed in the 3.5% NaCl solution. A propagation of the crack along grain boundaries was also observed at low da/dN-values in a constant-amplitude loading test (Fig. 6d). For the two alloys considered, the mechanisms in the low loading period were found to be most sensitive to the environment. It can be therefore concluded that the retardation is decreased because the crack propagation mechanism in the low loading period is highly sensitive to the test environment. The described tendencies are further corroborated by the observation that retardation at a crack length of 12 mm appeared more pronounced than at 3 mm crack length (compare Table 3). At 12 mm crack length, the change in the crack propagation mechanism was more distinct. However, if the amount of retardation is compared relatively to the increase in the aggressiveness of the environment, it is found that the retardation decreased more at 3 mm crack length than at 12 mm.

Until now, only the environmental influence on the crack propagation in the low loading period has been considered. There are strong indications that the crack propagation mechanism occurring during the high loading period influences the retardation behavior, as well. This indeed is the case and it has been shown in Refs 19 and 23. The changes in the crack propagation behavior at the high loading level may be mainly attributed to the fact that hydrogen does not only influence the crack propagation mechanisms, but also the ductility of the material just ahead of the crack tip. Albrecht et al. [24] and Hardwick et al. [25] respectively showed that hydrogen-charged 7000-series and 2000-series aluminium alloys showed a significant loss in their ductility. For both the alloys, the loss in ductility was most pronounced when they were in the underaged condition because of the high slip planarity. Welpmann et al. [26] tested an underaged aluminium alloy in both 3.5% NaCl solution and in air and found that the ductility (true fracture strain) decreased as the strain rate decreased. If the aluminium alloys used in this investigation were cycled in the three different test environments at a constant total strain range of $\Delta \epsilon = \pm 1\%$ and at a frequency of 0.1 Hz and were fractured in a tension test without a change of the test environment, a loss in ductility dependent on the number of strain cycles and the environment was found [27] (compare Fig. 13).

These results indicate a loss in ductility from hydrogen embrittlement, which reduces the amount of plastic deformations ahead of the crack tip. Therefore, the residual stresses ahead of the crack tip, which are a main cause for the retardation behavior in a high-low loading sequence, are reduced. The influence of the loss in ductility leads to a decrease in the crack opening stress level. The increase in the effective stress intensity as pointed out by several investigators [28-30] should give a simple explanation of the observed behavior. Less material ahead of the crack tip should result in smaller deformations in the wake of the crack and, consequently, to lower crack opening stress levels, which were observed. However, the actual investigation results are not unique. Schijve and Arkema [31] and Ewalds [32], for example, did not find any systematic influence of the environment on the fatigue crack closure under constant-amplitude loading conditions. As a reason, they argue that the plastic deformations before and behind the propagating crack tip are influenced by the environment and, therefore, no change in that balanced situation occurs. That does, however, not necessarily mean that the crack closure behavior and the retardation after a high-low loading



FIG. 13—True fracture strain in a tension test after N strain cycles in vacuum, air and in a 3.5% NaCl solution for (a) Al X-7075, 24 h at 100°C and (b) Al 2024-T3.

sequence is not dependent on the environment, as well, where the residual stress state ahead of the crack tip has additionally been taken into account [33].

Fatigue Crack Propagation After a High-Low Loading Sequence with a Change of the Environment

a. Change from Vacuum to Air or to a 3.5% NaCl Solution—In this situation the retardation in crack propagation increases (Fig. 4b) compared to those tests, where no change of the environment had occurred (Fig. 4a). This behavior may be explained as follows.

Along with changes in loading levels and environments, a change in propagation mechanism occurs from slip decohesion to the environmentally assisted mechanism of tensile decohesion. A change in the propagation mechanisms can also increase retardation. The initial deformations occur in vacuum where a high dislocation mobility exists and intense slip bands are formed. After changing the environments, hydrogen transport into the interior of the material is assisted by dislocations. This causes tensile decohesion (Figs. 10b-d).

The mechanism of dislocation transport of hydrogen becomes important at short crack lengths, where the crack propagates along intense slip bands in vacuum as well as in the 3.5% NaCl solution. In this case, virtually no retardation occurs (compare Table 3). This indicates that in spite of the differences in crack propagation mechanisms in different environments, the change in mechanisms has no influence on retardation behavior.

2. During the high loading period with a crack propagation in vacuum, the crack tip material exhibits a higher ductility (compare Fig. 13) than in the case with an aggressive environment. The plastic displacements ahead of the crack tip and behind the propagating crack are larger than in the NaCl or air environment. In the subsequent low loading periods, the aggressive environment exhibits higher residual stresses and a higher crack closure stress level can be expected. This leads to an increase in retardation.

b. Change from Air or 3.5% NaCl Solution to Vacuum—If the crack propagates in an aggressive environment during the high loading period and if the environment is then changed to vacuum, together with the drop in the loading level, the following behavior is observed (Fig. 4c).

1. The crack propagation in air at the high loading level leads to a considerably lower retardation after the drop in load. The observed behavior can be partially explained by the decrease in retardation during the vacuum period caused by fatiguing in air. This implies environmentally induced interaction between crack propagation and retardation behavior. The environmentally induced decrease in the ductility during the crack propagation on the low loading level in air and the changes in the elastic-plastic displacements before and behind the propagating crack and of the residual stresses due to the environment decrease the crack opening stress level and the retardation, as compared to tests with a constant vacuum environment at the high and at the low loading level. The equilibrium between the residual stresses induced by the plastic zone ahead of the crack tip and the residual plastic displacements on the fracture surface in the wake of the crack, which is present in a test with only one environment, is disturbed if the environment has changed, and is then visible in the differences in the crack propagation behavior.

2. If the high loading period is performed in the 3.5% NaCl solution, one would expect a decrease in retardation in vacuum after the change in the loading level and environment. But what is observed is a complete stop in crack propagation for about 1.5 million cycles. In this case, another type of crack propagation mechanism might be dominant, and this mechanism must be incompatible with the crack front. Therefore, a completely new reinitiation of the crack has to be required. In Fig. 12, the fracture surface is shown, after more than 1.5 million cycles at the low loading level in vacuum. To investigate the fatigue fracture surface that was generated on the high loading level in the 3.5% NaCl solution, the specimen was statically cracked. This revealed a large number of secondary cracks (Fig. 12*a*) and cracks in the boundaries between the matrix and the incoherent particles (Fig. 12*b*).

These observations coincide with those made by Kohlen [34] (Fig. 14), who observed the crack tip morphology with a special infiltration technique. On the replica taken from the crack front, he found secondary cracks and something similar to a "mushroom." He explained that the mushroom was formed when the infiltrating plastic floated into the gaps formed by the cracked boundaries between the matrix and the particle (Fig. 12b). From these observations, it is reasonable to assume that the irregular (particle boundary cracking) and branched (secondary cracks) crack front reduces the effective ΔK to such an extent that the crack propagation in the low load in the vacuum period is totally hindered.



FIG. 14—Scanning electron micrograph of the replica of the crack tip of a fatigue crack propagation specimen (Al 7075-T6) from a test performed in a 3.5% NaCl solution, by courtesy of A. M. Kohlen [34].

This is further substantiated by the results of the crack propagation tests with constant-amplitude loading, where only the environment was changed from the 3.5% NaCl solution to vacuum (compare Fig. 5). In this case, a retardation of crack propagation was observed after the change of the environment.

The Crack Length, a*, the Crack Length with Retardation

The affected crack length, a^* , varies with the environment in which the test was performed with the high-low loading sequence (Table 3a-c and Figs. 3a and b). It is very often assumed that a^* corresponds to the size of the plastic zone that is generated at the high loading level [35]. That means that the plastic zone size should be the largest in vacuum and the smallest in the 3.5% NaCl solution. There are indeed some indications that the extension of the plastic zone in vacuum is larger than in an aggressive environment [36]. A peak-aged aluminium alloy, X-7075, which contains precipitate free zones at the grain boundaries, shows in vacuum a change in the crack propagation mechanism from the slip-band-type mechanism to a propagation along grain boundaries at high da/dN and ΔK -values [7,19]. The change occurs earlier in vacuum, and hence at lower da/dN and ΔK -values than in air [37]. This fact is of some importance, because the plastic zone size and the transition to the grain boundary mechanism correlate to some extent [38]. The transition usually occurs when the size of the plastic zone is equal or higher than the diameter of a grain. Since the transition occurs earlier in vacuum, it indicates that the plastic zone in vacuum is larger than the environmentally influenced plastic zone. However, it is still difficult to find a direct correlation between the crack length with retardation a^* , observed after a high-low loading sequence with a parallel change of the environment, and the differences in the plastic zone size developed in the high loading level, because no systematic variation of a^* occurred. The results indicated that not only the plastic displacements performed in the high loading period influence a* but additionally the environment and the macro- and the micromechanics of crack propagation in the low loading period influence a^* .

In the following a straightforward explanation of the observed behavior is attempted.

Assuming that the plastic zone size is dependent on the environment and that a^* is a function of the plastic zone due to the maximum load in the last cycle at the high loading level, then a certain stabilized condition depending on the plastic deformation capability of the materials as a function of its true fracture strain and the resulting plastic displacements can develop, furthermore, if no change in the environment occurs during the whole test. The correlation between the plastic zone size and a^* remains undisturbed in a constant environment. The situation must change if the environment is changed along with the drop in the loading level. For example, if the high loading level is performed in vacuum and a change to air or 3.5% NaCl solution is performed, another stabilized condition under a constant environment must develop. The large plastic displacements that are formed during the high loading level in vacuum play an increasing effect on the number of delay cycles, N_D . As the load level and the environment change, the true fracture strain of the volume elements ahead of the crack tip are decreased, starting with the first cycles in the aggressive environment. The reduction in the true fracture strain leads to:

- 1. lower residual stresses during the cycles in the aggressive environment (the plastic displacements in the vicinity of the crack tip are predominantly influenced), and
- 2. a reduction of the true fracture strain of the material over the entire length of the large plastic zone that has been formed in the high loading level. This reduces the effect of the plastic zone area regarding its effect on the crack retardation.

Summary

1. The fatigue crack propagation behavior of the high strength aluminium alloys, 2024-T3 and X-7075, in an underaged condition was investigated.

The fatigue crack propagation under constant-amplitude loading is lowest in vacuum (10^{-4} Pa) followed by laboratory air and 3.5% NaCl solution.

Under a high-low loading sequence, a significant retardation in the fatigue crack propagation is observed, which is most pronounced in vacuum. The affected crack length, a^* , was the longest in vacuum and the shortest in the 3.5% NaCl solution.

A change from vacuum at the high loading level to air or 3.5% NaCl solution at the low loading level decreases the retardation and a^* . That implies that the plastic zone size at the high loading level is not the only parameter that controls a^* .

Under a change from laboratory air at the high loading level to vacuum at the low loading level, a considerable decrease in the number of delay cycles occurs. However, after a change from the 3.5% NaCl solution to vacuum, a crack arrest over more than 1.5 million cycles was observed.

2. The test environment has a considerable influence on a^* and N_D .

It was concluded that a^* not only depends on the size of the plastic zone that is developed during the high loading period and also on the environment present during the subsequent low loading period, while N_D is strongly dependent on the variations in the environment during the high-low loading sequences.

The effect of the environment can be mainly attributed to the following factors.

- a. Hydrogen influences the slip planarity within the plastic zone. In an aggressive environment, tensile decohesion during crack propagation is favored, whereas in vacuum, the slip decohesion is predominant.
- b. The ductility of the material in the vicinity of the crack tip is decreased because of hydrogen embrittlement. This alters the residual stresses and strains and, therefore, the crack opening stress level, and with that the retardation behavior.
- c. Other important environmentally influenced phenomena are the crack front morphology, which in vacuum is highly irregular, while in the 3.5% NaCl solution secondary cracking can be observed. The crack front morphology and the existence of the secondary cracks have a significant effect on the effective stress intensity.

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Environmental Influence on the Effect of a Single Overload on the Fatigue Crack Growth Behavior on a High-Strength Aluminum Alloy

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ABSTRACT: The delaying effect of a single overload on the 2024 T351 aluminum alloy covering a wide ΔK range has been studied in ambient air, secondary vacuum, and high purity nitrogen (N₂). It is shown that for a given environment and an overload ratio, the delay behavior can be rationalized in terms of the peak stress intensity factor corresponding to the overload for the studied test conditions. At low ΔK values, the overload effect is confined to a grain. The results obtained show that while the size of the overload affected zone is not affected by the environment, the number of delay cycles at an R ratio of 0.5 in vacuum can be ten times as high as that obtained in the two other environments. At an R ratio of 0.1, at low ΔK levels, the delaying effects can be similar in vacuum and in air. The observed effects are explained on the basis of mechanisms governing constant-amplitude crack growth behavior of the studied alloy.

KEY WORDS: fatigue crack propagation, overloads, delay, grain size, environmental effects, crack closure, micro-mechanisms, fatigue (materials), cracking

The effect of a single spike overload on the fatigue crack propagation has been the aim of several studies ever since Schijve [1] first showed that a fatigue crack can be considerably retarded following a peak load excursion [1-6].

Models that describe the retardation effect use different concepts to describe the crack growth rate reduction in the overload plastic zone, such as, empirical retardation factor [7], residual compressive stresses [8], crack tip blunting, [9] and crack closure [10].

In a recent study, the limitations of these models have been shown, and it has been proposed that crack tip micro-mechanisms, such as crack path deviation or crack branching, could play an important role in the post-overload crack growth behavior [11].

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Main Parameters

The main parameters governing the delaying effect due to an overload are (1) the overload ration, τ , the ratio of the peak stress to the baseline stress amplitude; (2) the baseline stress intensity factor range, ΔK_i ; and (3) the baseline stress ratio, R_i .

Overload Ratio, 7

It has been shown that there is a value of τ below which the overload causes no effect [2]. This minimum of τ depends upon the material, and a value of 1.3 has been reported for the 2024 T351 alloy [12]. Above this level, the delay induced by the overload increases with τ and there is a maximum value of this parameter above which an overload causes crack arrest [2]. This maximum is on the order of 2.3 [12] for 2024 T351.

Baseline Stress Intensity Factor Range, ΔK_i

For a given value of τ , the number of delay cycles, N_d (defined as the number of cycles necessary for the crack to reach its steady-state regime after the application of the overload), decreases with ΔK_i at low ΔK_i levels, while it increases with ΔK_i at high ΔK_i levels so that a U-shaped curve is obtained when N_d is plotted with respect to ΔK_i . It has been suggested that, at low ΔK_i levels, microstructural effects would be predominant, while high ΔK_i levels are characterized by a gradual development of plane stress state near the crack tip [13,14].

Five major types of delayed effect have been identified that can be described for increasing values of ΔK_i levels [14]:

- A. crack arrest,
- B. immediate retardation after the overload where the crack remains blocked for several thousand cycles before growing again at the pre-overload crack growth rate,
- C. a small acceleration just after the overload followed by a gradual decrease in crack growth rate to reach minimal growth rate after which the crack reaches the pre-overload growth rate almost immediately,
- D. the classical delayed retardation that is similar to the one in Type C except for a gradual crack growth reacceleration after the point of minimal growth rate, and
- E. a delayed effect similar to the one in Type D except for a second residual delay associated with large plastic zone sizes.

The evolution of the crack length, a, with respect to the number of cycles, N, and that of the crack growth rate, da/dN, with respect to the crack length, a, for these types of delay are schematically given in Fig. 1.

Baseline Stress Ratio, R_i

It has been reported that for a given baseline stress intensity level, ΔK_i , and an overload ratio, τ , the value of R_i is lower and the delayed number of cycles, N_d , is higher [2]. The overload effects are much lower for negative values of R_i [15].

Environmental Influence on the Retardation Effect

The effect of the environment on the overload related phenomena has received very little attention. However, the studies reported in Refs 16 and 17 have shown that the delay can



FIG. 1—Types of delay curves: Curves $A = \text{constant } \Delta P \text{ crack growth, and Curves } B = \text{crack growth}$ after an overload.

be much lower in humid environments as compared to dry environments on the 7075 T651 and the 2024 T351 alloys, and previous studies conducted on the 2024 T351 [18] have shown that in vacuum the delaying effects can be ten times as high as those observed in ambient air.

A correlation of the post-overload delayed behavior and of the near threshold behavior on 2024 T351 has been proposed to consider if the controlling micromechanisms could be the same in both cases [19]. This approach has been expanded recently [11,20].

The aim of this study is to give further experimental evidence of the environmental influence on the post-overload crack growth behavior based on tests conducted in vacuum, ambient air, and in high-purity nitrogen (N_2) covering a wide ΔK_i range. The study is augmented with observations of crack profiles and of crack tip plastic zones. Some microscopic details are illustrated by fractographic observations. The discussion that follows is intended to explain the micromechanisms involved, and suggestions are made on the validity of current models.

Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
Weight, %	0.1	0.22	4.46	0.66	1.5	0.01	0.04	0.02	remainder

TABLE 1—Nominal composition.

Experimental Details

The material used for this study was a 30-mm thick plate of the 2024 T351 alloy, quenched and aged at room temperature after a cold stretch of 1.5 to 3%. The microstructure consists of typical pancake-shaped recrystallized grains that average 190 by 60 by 70 μ m, and smaller unrecrystallized grains that average 45 by 25 by 28 μ m in size. The composition and nominal mechanical properties of this alloy are given in Tables 1 and 2, respectively.

Compact tension specimens 75 mm large and in two thicknesses of 4 and 10 mm were machined in the TL orientation. A computer-controlled servohydraulic machine equipped with an environmental chamber was used for the present tests. The environmental conditions were ambient air (about 50% relative humidity), high vacuum ($<5 \times 10^{-4}$ Pa) and purified nitrogen containing less than 3 ppm water (H₂O), 1 ppm oxygen (O₂), and 1 ppm C_nH_m.

The overloads were applied by computer control at a frequency of 0.02 Hz. The majority of the overload tests were carried out with a τ value of 2.0. On each specimen, at least five overloads were conducted at different ΔK_i levels at successive crack lengths. Care was taken to sufficiently separate the overloads to avoid cumulative effects.

The pre- and post-overload test frequencies were 35 Hz in vacuum and 20 Hz in air and in N₂. The values of R_i considered were 0.5 and 0.1.

The crack growth was optically monitored on the polished side of the specimens using a traveling microscope ($\times 25$). The crack growth rate was determined by the secant method [21].

The overload effect was characterized by the following parameters (Fig. 2):

- 1. the baseline conditions ΔK_i and R_i ;
- 2. the number of delay cycles, N_d ;
- 3. the number of cycles during which the crack is blocked, N_B , or the minimum growth rate reached after the retardation phase, $(da/dN)_{min}$; and
- 4. the crack length up to the point of arrest or of minimal growth rate, a^* , and the crack length affected by the overload, a_d .

The crack opening load was determined by the offset technique [22].

After the tests, the evolutions of the plastic zone and that of the crack profile were observed on an optical microscope using Nomarski interferometry [23], and microfracto-graphic observations were performed on the cracked surfaces.

Yield Strength,	Tensile Strength,	% Elongation (gage	Cyclic Yield Strength,
MPa	MPa	length, 30 mm)	MPa
300	502	11	500

TABLE 2—Average mechanical properties.



FIG. 2—Type of loading considered and definition of delay parameters.

Experimental Results

The experimental results, as defined in Fig. 2, are given in Table 3 for all the studied test conditions covering a wide range of ΔK_i , from 3 MPa \sqrt{m} to 18 MPa \sqrt{m} . For each test condition, the type of delay, as defined in Fig. 1, is also indicated.

In general, Type B behavior is observed for low ΔK_i values. However, certain exceptions are encountered in air and in N₂. In the case of $\Delta K_i = 5.67$ MPa \sqrt{m} at $R_i = 0.1$ in air, Type A is obtained, that is, complete crack arrest after the overload. This test was stopped after about $3 \cdot 10^6$ cycles after the overload, and the crack did not advance. In the case of N₂ and in the low ΔK_i regime, a gradual deceleration phase is observed before temporary crack blocking, and this type of delaying effect is called B'.

At moderate ΔK_i values, a Type C behavior is observed followed by Type D.

At very high ΔK_i values, a Type E behavior is observed and only for 4-mm thick specimens.

The Number of Delay Cycles

The relationship between N_d and ΔK_i for 10-mm thick specimens is given in Fig. 3a. This figure shows the considerable influence of the environment in the explored ΔK_i range. This result is consistent with what was previously observed in the same alloy for $\Delta K_i > 10$ MPa \sqrt{m} [18]. The delay in vacuum is an order of magnitude higher than in air, independent of

$\Delta K_i,$ MPa \sqrt{m}	$(da/dN)_i$, mm/cycle	K_{pic} MPa \sqrt{m}	N_d , cycles	<i>a</i> _{<i>d</i>} , mm	N_B , cycles	<i>a</i> *, mm	Туре
		ENVIRONMEN	TT = VACUUM,	R = 0.1, B =	10 мм		
5.7	8.0 E-7	12.0	1.8 E6	0.18	7.1 E5	0.04	В
8.0	2.4 E-6	16.9	8.2 E5	0.20	6.1 E5	0.04	В
9.0	6.6 E-6	18.9	4.8 E5	0.24	1.3 E5	0.04	В
10.0	2.0 E-5	21.1	2.0 E5	0.55		0.08	D
12.6	5.2 E-5	26.5	1.5 E5	1.6		0.30	D
15.7	2.0 E-4	33.0	3.6 E5	2.1		0.80	Ð
		ENVIRONMEN	T = VACUUM,	R = 0.5, B =	10 мм		_
5.6	8.0 E-7	16.9	8.8 E5	0.17	3.3 E5	0.04	B
7.3	1.1 E-5	21.9	2.8 E5	0.35	1.0 E5	0.07	В
8.9	5.0 E-5	26.6	9.4 E4	0.40	4.0 E4	0.05	В
10.0	1.4 E-4	30.0	7.3 E4	0.70		0.20	D
11.0	2.0 E-4	33.1	1.5 E5	1.0		0.34	D
		ENVIRONME	NT = VACUUM	R = 0.1, B =	4 MM		
7.9	3.0 E-6	16.7	5.5 E5	0.28	2.9 E5	0.04	В
10.0	2.0 E-5	21.0	2.1 E5	0.86	1.5 E4	0.07	В
12.0	4.6 E-5	25.2	1.3 E5	0.72		0.15	С
14.2	1.2 E-4	29.6	1.9 E5	2.5		0.30	D
15.7	2.0 E-4	33.1	2.9 E5	3.5		0.51	D
17.1	2.3 E-4	35.7	3.2 E5	3.5		0.60	E
		ENVIRON	MENT = AIR, R	= 0.1, в = 10	MM		
5.6	4.0 E-6	11.9	>2.8 E6		>2.8 E6		A
7.0	6.8 E-6	14.8	7.2 E4	0.18	2.3 E4	0.04	В
8.0	5.0 E-5	16.9	4.5 E4	0.52	1.3 E4	0.05	В
10.0	8.9 E-5	21.1	2.0 E4	0.33		0.15	C
12.6	2.2 E-4	26.5	1.5 E4	0.9		0.30	C
15.7	4.6 E-4	33.0	2.5 E4	1.7		0.70	D
2.0	2050	ENVIRON	MENT = AIR, R	= 0.5, B = 10	MM	0.02	n
3.0	3.0 E-6	9.0	8.4 E4	0.12	2.6 E4	0.03	В
4.8	6.3 E-6	14.5	5.2 E4	0.15	6.0 E3	0.03	В
5.6	1.4 E-5	16.9	4.7 E4	0.12	1.0 E4	0.03	В
7.0	7.0 E-5	21.1	1.9 E4	0.30		0.04	C C
8.0	1.1 E-4	24.0	1.4 E4	0.35	•••	0.06	C
11.0	3.0 E-4	33.0	1.9 E4	1.17		0.33	D
0.0	2055	ENVIRON	MENT = AIR, R	= 0.1, B = 4	MM	0.02	в
8.0	2.0 E-5	16.9	6.0 E4	0.30	3.3 E4	0.03	В
10.0	1.2 E-4	21.0	3.6 E4	1.2	2.0 E3	0.20	В
12.0	1./ E-4	25.2	2.4 E4	1.6	2.4 E3	0.27	В
14.0	3.4 E-4	29.6	2.4 E4	2.0		0.49	U D
15.7	3.2 E-4	33.1	3.4 E4	2.4		0.51	D
17.0	5.0 E-4	35.9	3.2 E4	2.7	•••	0.52	E
2.2	40 5 (ENVIRONMEN	T = NITROGEN	R = 0.5, B = 0.20	10 MM	0.04	D ′
5.2	4.0 E-6	9.5	5.0 E4	0.20	3.0 E4	0.04	B'
4.8	6.U E-6	14.0	4.0 E4	0.20	2.0 E4	0.06	B,
5.6	/.UE-0	17.0	3.0 E4	0.16	3.0 E4	0.09	U P
1.5	1./ E-3	22.0	3.0 E4	0.18	2.0 E4	0.05	В
9.2	1.6 E-4	21.5	1.8 E4	0.50	•••	0.07	
11.0	2.3 E-4	33.0	2.3 E4	0.90		0.22	U

TABLE 3—Test conditions and results.

 R_i and ΔK_i , except for the case of $\Delta K_i = 5.67$ MPa \sqrt{m} and R = 0.1 in air where the delay is at least equal to that observed in vacuum.

The U-shape of these curves is consistent with the description proposed in Refs 13 and 14 where N_d decreases with ΔK_i at low ΔK_i values to reach a minimum and the corresponding value of ΔK_i depends on R_i . The minimum delay is observed at higher ΔK_i for $R_i = 0.1$. It can also be observed that the U-shape is not so prominent in air and in N_2 at $R_i = 0.5$.



FIG. 3—(a) Evolution of the number of delay cycles with respect to ΔK_i for 10-mm thick specimens, and (b) normalization of delay behavior with respect to K_{pic} .

The results obtained in N₂ show that the delay in this environment is similar to the one in air at $R_i = 0.5$.

This behavior is better illustrated in Fig. 3b where the evolution of N_d is presented as a function of K_{pic} , the peak stress intensity factor corresponding to the overload. In this figure, it can be seen for both the studied thicknesses that the results obtained in air and in vacuum fall in two well-defined U-shaped curves independent of the R_i ratio. The results obtained in N₂ are merged with the ones in air. It can also be observed that minimum delay is observed for a particular K_{pic} value independent of the environment. This transitional level, determined as the average of what is observed in different test conditions, is equal to 26.7 ± 2.0 MPa \sqrt{m} . Based on these observations, it appears that for a given environment and overload ratio, the main controlling parameter is K_{pic} . The behavior in the N₂ environment is quite important, and it has been shown previously that the constant-amplitude fatigue crack growth behavior in this environment at high ΔK values is similar to the one in vacuum; while at low ΔK values, the behavior in N₂ is comparable to the one in air, well distinguished from the high growth rate regime by a well-defined transition as shown in Fig. 4. This transitional behavior is not observed for overload tests even though the ΔK_i range extends on either side of the plateau at a crack growth rate of ~5.10⁻⁶ mm/cycle.

The Number of Blocked Cycles and the Minimum Growth Rate Reached at the End of the Deceleration Phase, $(da/dN)_{min}$

The evolution of the number of blocked cycles, N_B (for Types B and B') with respect to $K_{\rm pic}$, is shown in Fig. 5. In this figure, the effect of the environment is also evident. In vacuum, the value of N_B decreases from about 5×10^5 cycles to about 4×10^4 cycles as $K_{\rm pic}$ increases from 12.6 to 23 MPa $\sqrt{\rm m}$.



FIG. 4—Constant-amplitude crack growth behavior in air and in high-purity N_2 at R = 0.5 compared to what is observed in vacuum.



FIG. 5—Number of cycles during which the crack is blocked after an overload for Type B delay expressed with respect to K_{pic} .

In air, except for the previously described test where crack arrest was observed, the value of N_B , in spite of a dispersion, is near constant at about 2.5 10⁴ cycles. In N₂, the value of N_B is also near constant at about the same value.

The evolution of $(da/dN)_{min}$ for the present tests is presented in Fig. 6. In vacuum, the value of this parameter varies gradually from about $4 \cdot 10^{-7}$ mm/cycle to about 10^{-6} mm/ cycle as K_{pic} increases. At the highest K_{pic} values considered, $(da/dN)_{min}$ tends to decrease. In air and in N₂, the value of this parameter is nearly constant at about $1 \cdot 10^{-6}$ mm/cycle for $K_{pic} \leq 18$ MPa \sqrt{m} , but for the test with crack arrest. It is interesting to note that this value is comparable to the da/dN level corresponding to the transition range shown in Fig.



FIG. 6—Minimum growth rate reached after the overload with respect to K_{pic} : same symbols as in Fig. 5.

4. For higher K_{pic} values, $(da/dN)_{min}$ increases to a maximum of about 10^{-5} mm/cycle before dipping at higher K_{pic} values.

The environmental effect is predominant at low K_{pic} values where $(da/dN)_{min}$ in vacuum is about 100 times as low as in active environments (but for the test in air with crack arrest). At moderate to high K_{pic} values, the difference between vacuum and other environments is characterized by a nearly constant factor of 10.

The Crack Growth up to the Point of Minimum Growth Rate, a^* , and the Total Crack Length Affected by the Overload, a_d

The evolution of these two parameters is shown in Figs. 7*a* and *b*, respectively, for the present tests. It can be seen that a^* is nearly constant at about 0.04 mm for $K_{\rm pic} \leq 20$ MPa \sqrt{m} . This distance is comparable to the size of unrecrystallized grains for the material used in this study. At higher values of $K_{\rm pic}$, a^* increases with $K_{\rm pic}$. It can also be seen that for



FIG. 7—(a) Crack length required to reach the minimum growth rate, a^* , as a function of K_{pic} : same symbols as in Fig. 5; and (b) total crack length affected by the overload, a_{d} , with respect to K_{pic} : same symbols as in Fig. 5.



FIG. 8—Comparison of da/dN versus ΔK_{eff} relationships obtained at constant-amplitude and overloads tests.

 $K_{\text{pic}} \ge 20 \text{ MPa } \sqrt{\text{m}}, a^*$ is greater for tests conducted at R = 0.1. No influence of environment is detected on this parameter.

A similar evolution is observed in the relationship between a_d and K_{pic} . For K_{pic} lower than ~20 MPa \sqrt{m} , the value of a_d is near constant and equal to about 0.2 mm, which is comparable to the size of recrystallized grains in the crack growth direction.

At higher values of K_{pic} , a_d increases with K_{pic} and a_d is generally slightly larger for tests conducted at R = 0.1. As before, no significant influence of the environment could be detected on this parameter.

The analysis of the evolution of the crack opening stress intensity factors, K_{op} , for overload tests was previously presented [24,25]. It has been shown that the evolution of K_{op} , as measured from compliance variations, can neither explain the delay behavior nor the environmental effect [25]. The relationship between da/dN and ΔK_{eff} (ΔK_{eff} being the effective stress intensity factor amplitude = K_{max} - K_{op}) for the present tests in vacuum is compared to constant-amplitude behavior in Fig. 8. Note that the results obtained after overloads are quite different from what is observed for constant-amplitude test conditions. Similar results have been previously reported for other alloys as well [26].

Discussion

The present results show that the effect of environment in the post-overload behavior depends on the test conditions such as ΔK level and the *R* value. Apart from the test conducted in air at $R_i = 0.1$ and $\Delta K_i = 5.67$ MPa \sqrt{m} , which shows a singular behavior, the environmental effects on the post-overload behavior can be summarized as follows.

- For comparable test conditions, the number of delay cycles in vacuum is an order of magnitude higher than those observed in air and in purified N₂ even though the overload affected zone remains practically independent of the test environment.
- 2. At very low K_{pic} levels, the environmental effect is highly marked; while in vacuum, N_d increases with decreasing K_{pic} independently of R_i , and in air and in N₂, a tendency for a stabilized N_d level is observed at low K_{pic} values, especially at an R_i value of 0.5.
- 3. A singular behavior is observed for the test conditions described that leads to crack arrest in air ($N_d \ge 2 \times 10^6$ cycles) that suggests a marked R ratio effect in air for overloads near threshold conditions.
- 4. In the overload affected zone, the number of blocked cycles (when observed) and the minimum growth rate reached are much lower in vacuum than in air and in N_2 .

These points are better illustrated in the delay curves obtained in vacuum, air, and N_2 at an *R* value of 0.5 shown in Figs. 9*a*, *b*, and *c*. Here, the main differences due to the environment are characterized by the minimum growth rate observed after the overload, which is much lower in vacuum.

The delay curves obtained in air and in N_2 are very similar. It is apparent from these figures that even if the pre-overload growth rate can be slightly different, the delay behavior is similar in these two environments marked by a minimum da/dN value that is near constant for all the test conditions.

These environmentally influenced differences with respect to the post-overload behavior can be explained based on the mechanisms invoked for describing the constant-amplitude behavior.

Comparing ambient air and vacuum (considered here as an inert environment), the environmental effect is attributed to water vapor adsorption and subsequent hydrogen embrittlement [27,28].

The N₂ atmosphere used in this study (containing traces of H₂O) constitutes an intermediate environment. The transitional behavior for constant-amplitude test conditions (Fig. 4) in this atmosphere, for a crack growth rate of about 5×10^{-6} mm/cycle, has been attributed to a gradual appearance of the previously mentioned environmental effect that depends on partial pressure of water vapor and the time available for water vapor transport and time for dislocation dragging in the process zone [27,28]. Above this growth rate in N₂, these particular conditions are not present and hence the crack growth behavior is similar to that obtained in vacuum. At lower growth rates after the transitions, the time available is sufficient for the effect to be activated because the crack growth is intermittent, according to a step-by-step mechanism [29,30].

For conditions existing at the crack tip after an overload and specifically at low ΔK_i values, the following analysis is proposed.

In the explored ΔK_i range, the higher retardation in vacuum can be mainly related to lower growth rates observed in this environment compared to active environments as observed near threshold conditions.

Considering that the post-overload crack propagation behavior is governed by similar mechanisms governing the near threshold behavior [11,19], one can expect lower growth rates in vacuum after an overload. Figure 10 illustrates the fracture surface observed after an overload conducted at a ΔK_i level of 5.67 MPa \sqrt{m} showing the existence of a Stage I crack growth with a crystallographic aspect. A similar mode of cracking has been observed near threshold for this alloy [29]. Beginning at moderate ΔK levels and for decreasing ΔK conditions, Stage II to Stage I is observed for aluminium alloys [27], resulting in a large decrease in growth rates. This mechanism alone can explain the large increase in N_d observed near threshold in vacuum, which is about 4.5 MPa \sqrt{m} (Fig. 4). The size of the crystallo-



FIG. 9—(a) Delay curves obtained at $R_i = 0.5$ in vacuum, (b) delay curves obtained at $R_i = 0.5$ in air, and (c) delay curves obtained at $R_i = 0.5$ in N_2 .



FIG. 10—Crystallographic crack growth for an overload test in vacuum, $\Delta K_i = 5.67 MPa \sqrt{m}$.

graphic step is on the order of the grain size. So, at low ΔK_i , it can be suggested that the overload leads to a decrease of the strain amplitude due to blunting or due to strain hardening [9,31] in the grain just ahead of the overload application point. Crack blocking observed after the overload (Fig. 5), at low ΔK_i levels would then correspond to the number of cycles necessary for the crack to cross this grain.

In active environments, a similar mechanism can be considered. But water vapor embrittlement has been shown to prolong Stage II environmentally assisted cracking [27] resulting in higher growth rates with respect to vacuum at low ΔK levels. This mechanism alone can explain lower delays in active environments.

Moreover, the minimum growth rate after the overloads is nearly constant at about 2×10^{-6} mm/cycle, that is, at a growth rate comparable to the transition plateau observed at constant-amplitude test conditions (Fig. 4). This transition plateau has been correlated to the occurrence of hydrogen embrittlement even in the presence of traces of water vapor [27,29]. Hydrogen assisted cracking has been shown to be time dependent. So crack growth in these conditions is mainly time-controlled and quite independent of the stress intensity factor. This mechanism can explain the near constant minimum growth rate and near constant N_d in air and in N₂ at an R value of 0.5.

In air, at an R value of 0.1, the presence of an oxide layer that acts as a water vapor trap that impedes the access of active molecules to the crack tip can explain complete crack arrest observed at a ΔK_i value of 5.67 MPa \sqrt{m} [27,32].

The transition between the left-hand side and the right-hand side of the U-shaped curve (Fig. 3b) is marked by minimum delay, and it is interesting to note that the test conditions (R value and the overload ratio) correspond to tests usually conducted to compare alloys used in the aircraft industry.

The present tests show that this transition is marked by Type C delay where the crack decelerates up to a minimum growth rate over a distance corresponding to the grain size, following which it reaches its pre-overload growth rate immediately. Figure 11 shows the



FIG. 11—Decohesion around inclusions observed for Type C delay behavior, $\Delta K_i = 10 MPa \sqrt{m}$ in air.

fracture surface obtained under such conditions, and it is marked by decohesion along the grain boundaries, which would indicate the existence of a critical strain level in the grain immediately ahead of the crack tip. The behavior of the crack at high ΔK values have been shown to be dependent upon the reduction of the equivalent stress intensity level in the overload plastic zone, and it was also shown that the effect of the environment is related to inherent differences in the material behavior [18,19].

Conclusions

The effect of the environment on the post-overload behavior depends on the R value and the ΔK level.

In general, the delay is maximum in vacuum as compared to air and high purity N_2 .

Even though the size of the overload affected zone shows no environmental effect, the delay behavior within this zone depends on the environment and R value.

The mechanisms used to explain the constant-amplitude crack growth behaviors can describe qualitatively the observed effects in the overload affected zone.

At low ΔK levels, the presence of traces of water vapor can lead to very low delay in an inert gas environment and the post-overload behavior is similar to that in ambient air at an R value of 0.5.

The presence of an oxide layer at low R values can lead to very high delay in air at R = 0.1 near threshold conditions.

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Test Methods

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Evaluation of K_{ISCC} and da/dtMeasurements for Aluminum Alloys Using Precracked Specimens

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ABSTRACT: The results of an interlaboratory program conducted to evaluate variability in measurements of the threshold stress intensity factor (K_{ISCC}) and stress corrosion crack growth rates (da/dt) for aluminum alloys are summarized. Precracked specimens machined from 7075-T6 aluminum alloy plate are exposed to a 3.5% NaCl (sodium chloride) solution by eleven participating laboratories. The effects of specimen configuration, starting stress intensity level, precracking procedure, and surface grooving are statistically evaluated, and sources of both interlaboratory and intralaboratory variability are identified. Data analysis indicates that variations in crack growth rates were related to difficulties associated with visual crack length measurements, especially on face-grooved specimens, and that more effective measurement techniques would more accurately characterize stress corrosion crack growth. In addition, test duration should be determined systematically, accounting for crack length measurement resolution, time for crack arrest, and experimental interferences. Variations in KISCC were related to the procedure used to measure the final bolt load. Final load measured by specimen reloading did not correlate well with that determined by compliance and appeared sensitive to factors such as corrosion product wedging and metallurgical features on the stress corrosion crack faces. Miniature instrumented load cells were used in several tests in a parallel program to monitor load relaxation during specimen exposure and to provide an indication of final load prior to specimen reloading. The load cell output during specimen exposure indicated that perturbations observed in crack length versus time curves may be related to real changes in load and should not be considered due only to crack length measurement difficulties. Compliance solutions were experimentally determined for both modified compact and double-beam wedge loaded specimens with different face-groove geometries and the results compared with published solutions. Both crack-mouth and load-line crack opening displacements were measured, and the data were used to define a relationship to correlate deflections at these measurement locations. The resulting relationship is compared with a previous solution determined by boundary collocation. No significant statistical variation in K_{ISCC} was observed with regard to specimen type, surface grooves, or specimen orientation, indicating both specimen configurations are suitable for stress corrosion testing and differences in $K_{\rm ISCC}$ determination were attributed to test procedures. Results of both the interlaboratory program and the additional studies should provide important contributions toward the development of a standard test method for stress corrosion testing and analysis using precracked specimens.

KEY WORDS: fatigue (materials), cracking, environmental effects, stress corrosion cracking, precracked specimens, fracture mechanics, modified compact bolt-loaded specimen, double-beam bolt-loaded specimen, aluminum alloys

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Nomenclature

- a Crack length, m
- B Specimen thickness measured on smooth faces, m
- B_n Specimen thickness measured at base of machined side notches, m
- COD Clip-on crack-mouth opening displacement gage
- da/dt Crack growth rate, m/s
- $DB(W_b)$ Abbreviation for double-beam bolt-loaded specimen
 - E Tensile modulus of elasticity, Pa
 - F Denotes fatigue precracked test condition
 - G Denotes face-grooved specimen
 - H One half the $DB(W_b)$ specimen height, m
 - $K_{\rm I}$ Stress intensity factor for Mode I failure, MPa-m^{1/2}
 - $K_{\rm IC}$ Plane strain fracture toughness, MPa-m^{1/2}
- $K_{\rm H}$, $K_{\rm L}$ High and low target starting stress intensity levels for environmental exposure, respectively, MPa-m^{1/2}
 - $K_{\rm ISCC}$ Threshold stress intensity factor level for stress corrosion cracking, MPa-m^{1/2} M Denotes mechanical precracked test condition
- $MC(W_b)$ Abbreviation for modified compact bolt-loaded specimen
 - P Specimen bolt load, N
 - $P_{\rm f}$ Final specimen bolt load
 - RBA Rigid bolt analysis
 - S Denotes smooth-face specimen
 - t Exposure time, s
 - $2V_{11}$ Total crack opening displacement at the load line, m
 - $2V_0$ Total crack-mouth opening displacement, m
 - W MC(W_b) specimen dimension from the load line to the back edge of the specimen, m
 - \overline{X} Statistical mean

Stress corrosion cracking (SCC) of aluminum alloys has long been recognized as a significant contributor to environmentally assisted failures in structural applications [1-4]. The ranking of SCC susceptibility in structural aluminum alloys as estimated from currently standardized test procedures is at best only qualitative [5]. These standards have been developed for smooth specimen techniques and provide only time-to-failure data. More quantitative evaluation of material susceptibility can be made by using fracture mechanics precracked specimens [6-10]. There has been much characterization done with various precracked specimen configurations but there is little agreement among researchers concerning test controls. As such, a widespread, accepted standard for stress corrosion evaluation using precracked specimens has not been developed.

The development of a standard test procedure requires thorough evaluation of potential specimen configurations and analyses, as well as an evaluation of the possible effects of each test variable. An interlaboratory program was conducted to evaluate the effect of several test variables on measured values of threshold stress intensity factor for stress corrosion cracking, $K_{\rm ISCC}$, and crack velocity, da/dt, as a function of stress intensity level, $K_{\rm I}$. This program was jointly planned and sponsored by ASTM Committees G1.06 on Corrosion of Metals and E24.04 on Fracture Testing and was designed to compliment an earlier interlaboratory program conducted with 4340 steel [11]. The overall objective of this test program was to develop supporting information for the preparation of a "recommended test procedure" for measuring $K_{\rm ISCC}$ and da/dt for aluminum alloys subjected to sustained loading in a corrosive environment. The specific program objectives were as follows:

- 1. to develop and evaluate test procedures designed to measure $K_{\rm ISCC}$ and da/dt under controlled conditions, and
- 2. to evaluate both interlaboratory and intralaboratory variability in measurements of $K_{\rm ISCC}$ and da/dt under prescribed conditions for each type of specimen and between different types of specimens.

The experimental program was initiated in 1982 and involved testing of commercially processed 7075-T651 aluminum alloy plate in 3.5% NaCl (sodium chloride) at room temperature under open-circuit (or freely corroding) conditions. Alloy 7075 was selected because of its well-documented high susceptibility to intergranular stress corrosion cracking in the peak aged condition [1,2,9]. Rolled, extruded, and forged product forms of this material are most sensitive to SCC damage when applied stress is in the short transverse direction. Under this loading condition, the elongated grain structures associated with these product forms provide preferential paths for large amounts of stress corrosion crack growth.

Precracked specimen configurations were selected for the advantage of analysis with linear elastic fracture mechanics. The test program was based on a factorial experiment design with four variables; specimen configuration, method of precracking, surface grooving, and starting stress intensity level; each having two levels. The factorial test is statistically designed to avoid replication of test conditions and allows evaluation of test variables with a minimum number of specimens. A constant deflection, K-decreasing test was conducted with modifiedcompact (MC(W_b)) and double-beam (DB(W_b)) bolt-loaded specimens (Fig. 1) exposed for 2000 h. Specimens at one laboratory were exposed for 9000 h to provide additional data regarding load decay and crack arrest in these specimens. Specimens were distributed to 14 laboratories, and of these, 11 completed testing and delivered results to the program coordinator. Nine of the laboratories conducted the full factorial test program with both specimen configurations and two laboratories elected to test only the half factorial test program with $DB(W_b)$ specimens. Miniature load cells were employed on additional specimens at one laboratory to monitor load decay behavior during stress corrosion crack growth. Additional studies involved evaluation of available stress intensity solutions and experimental determination of compliance relationships for each specimen configuration.

Materials, Specimens, and Procedures

Materials and Specimens

All test specimens used in the interlaboratory program were machined from a 6.35-cmthick plate of Aluminum Alloy 7075-T651 that was donated by Alcoa laboratories. Short transverse mechanical properties of the plate included yield strength of 433 MPa, ultimate strength of 501 MPa, elongation of 2.9%, and plane strain fracture toughness, $K_{\rm IC}$, of 22.53 MPa-m^{1/2}. The MC(W_b) and DB(W_b) bolt-loaded specimens were machined in two configurations, one with smooth faces, as shown in Fig. 1, and the other having 5% thickness Vshaped face grooves. Specimens were machined from the mid-thickness of the plate in the *S-L* orientation; that is, such that loading was in the short transverse direction with crack growth in the longitudinal direction.

Procedures

Specimen Precracking—Specimens were precracked by either fatigue cycling at low stress intensity levels or by mechanical overload (pop-in) to initiate a crack 0.25 to 0.38 cm beyond the chevron notch and then bolt loaded to one of two target starting stress intensity levels,



FIG. 1—Modified compact and double-beam precracked specimen configurations tested in the current study.

 $K_{\rm H} = 19.78$ or $K_{\rm L} = 13.19$ MPa-m^{1/2}. Stress intensity levels during fatigue loading were limited to two thirds of the starting stress intensity for environmental exposure. The stress intensity solution for the DB(W_b) specimen is based on an exact solution by Fichter [12] and is given by

$$K_{\rm I} = \frac{Pa}{B(H)^{3/2}} (12)^{1/2} \left(1 + 0.673 \frac{a}{H}\right)$$

The solution is a function of crack length, a, defined as the distance from the center of the loading bolts to the crack tip, the specimen bolt load, P, which can be determined by compliance from the load-line displacement, $2V_{11}$, and specimen geometry. The solution for the MC(W_b) specimen was developed by Newman [13] from boundary collocation and is given by

$$K_{\rm I} = \frac{P}{B(W)^{1/2}} \frac{\left(2 + \frac{a}{W}\right)}{\left(1 - \frac{a}{W}\right)^{3/2}} C_3\left(\frac{a}{W}\right)$$

where

$$C_{3}\left(\frac{a}{W}\right) = 1.31 + 5.28\left(\frac{a}{W}\right) - 19.67\left(\frac{a}{W}\right)^{2} + 24.57\left(\frac{a}{W}\right)^{3} - 10.27\left(\frac{a}{W}\right)^{4}$$

This solution again is a function of crack length, bolt load, and specimen geometry. Newman's $MC(W_b)$ solution accounts for crack line loading and load concentration effects, and both solutions allow for proportional scale up of specimen dimensions.

Computer control was used to monitor the fatigue precrack length during cycling by using experimentally determined compliance relationships of the form $a/W = fn(EB2V_0/P)$ for the MC(W_b) specimen and $a/H = fn(EB2V_0/P)$ for the DB(W_b) specimen. The quantity, B, is replaced by $(BB_n)^{1/2}$ for the face-grooved specimen configuration. During fatigue precracking a clip-on crack-mouth opening displacement (COD) gage was used to measure the displacement, $2V_0$. Visual measurements made to verify the final precrack length agreed with values estimated by the current experimentally determined compliance solution to within 2%.

Mechanical precracking resulted in crack-tip stress intensity levels greater than the starting target values for environmental exposure. Mechanically precracked specimens targeted for exposure at $K_{\rm H}$ were left at these higher K values. Mechanically precracked specimens targeted for testing at the low starting stress intensity were particularly unloaded to the $K_{\rm L}$ value. This unloading resulted in a compressed plastic zone at the crack tip. As SCC requires the application of a sustained tensile stress, this condition was included to evaluate whether any corrosion products produced during crack incubation could generate wedging forces sufficient to exceed the compressive stresses and initiate a stress corrosion crack.

Environmental Exposure—Specimens were continuously immersed in a 3.5% NaCl solution in controlled temperature and humidity. The solution was acetate buffered to pH = 4and dichromate inhibited to reduce the amount of general corrosion of the specimen surface [9] and control corrosion product accumulation in the advancing crack. Specimens were removed from solution at periodic intervals during the 2000-h test and crack lengths measured visually on each surface with a traveling stage microscope. This crack length versus time data was used to determine crack growth rate, da/dt. A stress intensity value was calculated for each measured crack length, and the combined data was plotted to determine the SCC crack growth rate as a function of calculated stress intensity.

At test termination, crack-mouth displacement, $2V_0$, was measured with a COD gage as the loading bolts were removed. Final specimen load, P_i , was indirectly measured by reloading the specimen to the measured displacement in a mechanical test machine. Specimens were fatigue cycled to mark the end of the stress corrosion crack, and then loaded to failure in tension to expose the crack faces. An accurate measurement of final crack length, a_i , was made by averaging five measurements across the specimen width. A final stress intensity value, $K_{\rm If}$, was calculated based on P_i and a_i .

Results and Discussion

Stress Intensity and Displacement Expressions—The stress intensity solutions developed by Newman and Fichter for the $MC(W_b)$ and $DB(W_b)$ specimen configurations, respectively, were generally found to be in good agreement with other published solutions. Fichter presents a correlation of his solution with others available in the literature [12]. These solutions were determined for other double-beam specimen configurations subjected to splitting forces, and while each of these solutions required prior assumptions about the functional relationship between K and a/H, Fichter's solution makes no prior assumptions. The solutions generally agreed to within 2%, but Fichter presents his solution to be the most accurate expression of the functional relationship between K and a/H [12]. Newman's solution for the MC(W_b) specimen agreed within 1% with solutions developed by Lefort and Mowbray [14] with finite element analysis and by Novak and Rolfe [15] with a fracture mechanics based three-dimensional analysis.

Compliance values, $2V_0/P$, were experimentally determined for both smooth-faced and face-grooved specimens with crack length ranges 2.0 < a/H < 8.0 and 0.3 < a/W < 0.8 for the DB(W_b) and MC(W_b) specimens, respectively. The resulting compliance solutions are given by

 $DB(W_b)$:

smooth face:
$$\frac{EB2V_0}{P} = \exp\left[4.32 + 1.32\left(\ln\frac{a}{H}\right) + 0.39\left(\ln\frac{a}{H}\right)^2\right]$$
face grooved:
$$\frac{E(BBn)^{1/2}2V_0}{P} = \exp\left[4.34 + 1.26\left(\ln\frac{a}{H}\right) + 0.41\left(\ln\frac{a}{H}\right)^2\right]$$

 $MC(W_b)$:

smooth face:
$$\frac{EB2V_0}{P} = \exp\left[8.23 + 13.98\left(\ln\frac{a}{W}\right) + 20.98\left(\ln\frac{a}{W}\right)^2 + 16.84\left(\ln\frac{a}{W}\right)^3 + 5.37\left(\ln\frac{a}{W}\right)^4\right]$$

face grooved: $\frac{E(BBn)^{1/2}2V_0}{P}$

$$= \exp\left[8.05 + 12.73\left(\ln\frac{a}{W}\right) + 17.71\left(\ln\frac{a}{W}\right)^{2} + 13.11\left(\ln\frac{a}{W}\right)^{3} + 3.80\left(\ln\frac{a}{W}\right)^{4}\right]$$

The experimentally determined solutions were compared with solutions developed by Newman through boundary collocation for the $MC(W_b)$ specimen, previously [13], and for the $DB(W_b)$ specimen for this study. The $MC(W_b)$ solution was also compared with other solutions found in the literature. Compliance data for the $DB(W_b)$ specimen configuration are summarized in Table 1. The solutions developed from experimental data differed from Newman's approximation by less than 2% for the smooth-face specimen and less than 4% for the face-grooved specimen for 2.0 < a/H < 8.0. Compliance values predicted for the smooth-faced and face-grooved specimens by the experimentally determined solutions agreed to within 3% for all a/H values. No other compliance solutions were available for the $DB(W_b)$ specimen.

Compliance data for the $MC(W_b)$ specimen are summarized in Table 2 for the range of crack lengths given by 0.3 < a/W < 0.8. Compliance values from the current experimentally determined solutions are given for the smooth and grooved geometries and are compared with results from Newman's boundary collocation study. Compliance solutions were developed both experimentally and by finite element techniques by Lefort and Mowbray [14]
a/H	Curren		
	S	G	Collocation
2.00	226.41"	223.71*	214.02
3.00	513.31	502.25	516.58
4.00	991.69	967.46	1012.95
5.00	1727.92	1685.66	1751.43
6.00	2799.45	2734.99	2780.13
7.00	4295.67	4206.31	4147.09
8.00	6318.60	6204.11	5900.32

TABLE 1—Compliance (EB2V_o/P) for the $DB(W_b)$ specimen configuration determined experimentally and by boundary collocation in the current study.

^a Experimental, S.

^b Experimental, G.

and Novak and Rolfe [15] and are also presented for comparison. The solutions developed by boundary collocation and finite element agreed very well, with differences in predicted compliance within 3% at higher a/W values. The solutions determined experimentally in this study predicted compliance values that agreed within 2% for the smooth-faced and facegrooved specimen geometries. These solutions agreed with Newman's solution fairly well, especially at the higher a/W values. Comparison of the current experimental solutions with those determined in the referenced works indicated variations in compliance ranging from less than 1% to nearly 10%. These differences in experimental results may be due to the methods used to simulate an advancing crack. In the current analysis, a 1.52-mm slot was incrementally advanced by electric discharge machining, while Novak and Rolfe [15] incrementally advanced a 60- μ m sawcut, and Lefort and Mowbray [14] advanced a crack by fatigue cycling.

Newman's boundary collocation analysis includes an expression that correlates specimen displacements at the crack mouth, $2V_0$, and the load line, $2V_{11}$, for both the MC(W_b) and DB(W_b) specimen configurations. Load line displacements calculated with this relationship at the start of environmental exposure are the basis for subsequent stress intensity calculations using rigid-bold analysis. Values of $2V_0$ and $2V_{11}$ were measured during the current

	Current Study			Lefort and Mo	owbray	Novak and Rolfe		
a/W	S	G	Newman	Finite Element	G	Finite Element	G	
0.30	40.61ª	32.87	26.98 ^c	30.95	34.22 ^b		29.50	
0.40	47.71	47.25	42.23	46.55	45.37	42.59	44.18	
0.50	70.19	67.99	64.76	68.80	67.00	65.03	66.77	
0.60	108.22	109.11	102.47	106.54	105.45	100.98	102.79	
0.70	187.82	197.24	182.57	186.98	183.54	173.30	177.90	
0.80	395.96	396.46	413.87	408.14	397.51	399.71	471.15	

TABLE 2—Compliance (EB2V_o/P) for the MC(W_b) specimen configuration determined experimentally in the current study and from published data.

^a Experimental, S.

^b Experimental, G.

^c Boundary collocation.

experimental compliance evaluation for both specimen configurations. The experimental measurements agreed with Newman's analysis to within 2% for the $DB(W_b)$ specimen configuration but only within 10% for the $MC(W_b)$ specimen configuration. A previous correlation suggested by Novak and Rolfe [15] for the $MC(W_b)$ specimen, based on proportional deflection of stiff beams about the crack tip as a pivot point, did not agree well with the experimentally generated data.

Interlaboratory Results—Although the interlaboratory program was based on a factorial experiment design, analysis by the appropriate statistical techniques was not possible due to the large number of specimens exposed at conditions that deviated from the test instructions. Specimens designated for mechanical precracking followed by exposure at high starting stress intensity were partially unloaded by several participants, indicating the test instructions did not clearly explain the loading procedure or emphasize the reason for including this test condition. Variations in starting stress intensity, K_{10} , levels occurred for specimens exposed at equivalent conditions by different laboratories, but these variations were likely due to inherent material variability. Greater variations in K_{10} were observed for the mechanical precrack and high starting stress intensity test conditions, which might be expected due to the greater amounts of plastic deformation associated with these variables.

Crack length versus time data is shown in Figs. 2 and 3 for each factorial test condition for both the $MC(W_b)$ and $DB(W_b)$ specimens, respectively. These curves are the results from one laboratory but represent typical results. The data does not exhibit the smooth, decreasing-slope curve usually shown schematically but rather contains several inflection points. The perturbations in the curve may be due in part to difficulties reported by several participating laboratories associated with visual crack length measurements on the specimen surfaces, especially on the face-grooved specimens, or may represent intermittent acceler-



FIG. 2—Crack growth record for $MC(W_b)$ specimens for each factorial test condition, where S and G indicate smooth-faced and face-grooved specimens, F and M indicate fatigue and mechanical precracking, and K_L and K_H indicate low and high starting stress intensity, respectively.



FIG. 3—Crack growth record for $DB(W_b)$ specimens for each factorial test condition, where S and G indicate smooth-faced and face-grooved specimens, F and M indicate fatigue and mechanical precracking, and K_L and K_H indicate low and high starting stress intensity, respectively.

ations due to corrosion product wedging. Corrosion product wedging can generate selfloading forces sufficient to exceed the intended bolt load [16]. Some curves exhibit increasing slopes at test termination, which may again represent accelerations due to corrosion product wedging.

The curves in Figs. 2 and 3 exhibit positive slopes near the end of the test, indicating crack arrest was not achieved during specimen exposure, and consequently the final stress intensity values calculated were not threshold values. Crack arrest was defined in the test procedure as a crack growth rate lower than 10^{-6} cm/h. Final crack growth rates after 2000 h exposure were typically 10^{-4} cm/h or greater. Examination of these curves reveals both the crack growth rate and the amount of crack growth at a given time is greater for the high stress intensity specimens for both specimen configurations. In addition, the final da/dt was greater for the specimens exposed at high starting stress intensity levels for both specimen configurations, indicating the high stress intensity specimens are even farther from crack arrest at 2000 h than the low starting stress intensity specimens.

The $MC(W_b)$ specimens exposed for 9000 h exhibited crack arrest after about 4000 h for the fatigue precracked test cases and for the mechanically precracked specimens exposed at high starting stress intensity. Fatigue precracked $DB(W_b)$ specimens exposed at K_L reached crack arrest in about 4000 h, but those exposed at K_H displayed an interim arrest at 4000 h, and then experienced additional crack growth. Two mechanically precracked specimens exposed at high starting stress intensity displayed very different behavior, with crack incubation times of 300 and 2000 h, and crack arrest times of 1500 and 6000 h for Specimens 1 and 2, respectively. This behavior is likely due to variations in plastic deformation associated with the mechanical precracking technique. Mechanically precracked $MC(W_b)$ and



FIG. 4—Photomicrographs of fractured $MC(W_h)$ specimens illustrating variations in surface delaminations, crack front morphology, and corrosion product accumulation during stress corrosion crack growth.

 $DB(W_b)$ specimens that were partially unloaded did not exhibit crack growth during the 9000-h exposure time.

Fracture surfaces of several specimens are shown in Figs. 4 and 5 for the $MC(W_b)$ and $DB(W_b)$ specimen configurations, respectively, and illustrate the variations in SCC morphology observed in this program. Crack growth remained generally planar for all test conditions, as would be expected for specimens loaded in the S-L orientation. Surface grooves were not necessary in these specimens to confine the crack to the midplane of the specimen, however, they may be necessary for specimens machined in other orientations. Metallographic sections indicated the cracks were intergranular and followed grain boundaries elongated in the longitudinal direction. Crack branching occurred in all specimens to some degree, resulting in the small delaminations seen on each fracture surface. In several specimens, branching resulted in changes in the plane of the crack, but the overall crack growth direction remained constant. Changes in crack plane occurred in a high percentage of the $MC(W_b)$ specimens, and were more common and more severe in the mechanically precracked specimens. Crack plane changes occurred to a lesser extent in the $DB(W_b)$ specimens and were usually associated with mechanical precracking. Crack fronts exhibited very little tunneling, with exceptions noted in some of the specimens that exhibited crack plane changes. The degree of corrosion product buildup varied widely, but was associated with the laboratory and not with test variables, and may be related to variations in solution chemistry and environmental conditions between laboratories.

Final load determined by specimen reloading at completion of the environmental exposure was found to be significantly different from that predicted by rigid-bolt analysis (RBA), and is likely due to crack closure effects caused by mismatch of the stress corrosion crack region



FIG. 5—Photomicrographs of fractured $DB(W_b)$ specimens illustrating variations in surface delaminations, crack front morphology, and corrosion product accumulation during stress corrosion crack growth.

and corrosion product wedging. Miniature load cells were placed between the faces of the loading bolts in several additional test specimens at one laboratory to investigate the source of this difference. These specimens were loaded to very high initial stress intensity values, and the load decay was monitored during stress corrosion crack growth. A plot of crack length and load cell output versus time is shown in Fig. 6. The changes in load cell output parallel crack growth events quite well, indicating the perturbations in the typical crack length versus time curve may be real and should not be attributed only to errors in crack length measurement. In some cases, the load calculated by RBA was within 5% of the load cell output, but in other cases, the difference was as large as a factor of two. This may be due to large regions of plasticity introduced at the crack tip by inadvertent mechanical overloads that occurred during bolt loading in these tests. The final bolt load determined by specimen reloading, P_i , was always substantially less than the final load indicated by the load cell, which would be expected if the crack is not fully closing on specimen unloading. For specimens in which the load indicated by the load cell and that calculated by RBA during specimen exposure agreed within 2%, the final load determined by specimen reloading differed by nearly 40%, suggesting that the reloading technique needs additional analysis and refinement.



FIG. 6-Variation in specimen load with time during stress corrosion crack growth.

Records of specimen reloading to failure are shown for several $MC(W_b)$ and $DB(W_b)$ specimens in Figs. 7*a* and *b*, respectively. The amount of crack growth, Δa , which occurred for each test case during stress corrosion cracking is shown beside each curve, and increases from left to right. Each curve exhibits a nonlinear region at small values of load and becomes linear well before specimen failure. This region of nonlinearity represents the crack closure effects discussed earlier. Both specimen configurations exhibit more nonlinear behavior during reloading for cases of greater stress corrosion crack growth. This may be due to the larger area over which corrosion product wedging and delaminations may be effective.

Final stress intensity, $K_{\rm If}$, values shown in Fig. 8 are averaged for each test condition for data received from the laboratories participating in the interlaboratory program. Data for the $DB(W_b)$ specimens represents results from eleven laboratories, and data for the $MC(W_b)$ specimens represents results from nine laboratories. The $K_{\rm If}$ values presented were calculated based on final load determined by specimen reloading, $P_{\rm f}$, and by RBA based on load-line displacement, with crack length determined based on an average of five measurements across the fracture surface. Measured values of $P_{\rm f}$ are sensitive to corrosion product wedging and crack surface morphology. The assumption that the loading bolts are rigid in RBA is not exact, but the bolts selected were significantly stiffer than the specimen, consequently, the error associated with RBA should be much smaller than that associated with the reloading technique. The effect of each test variable on final stress intensity values can be evaluated by examining Fig. 8. The effect of specimen configuration is observed by making an overall comparison for each group of bars. The K_{II} values calculated by RBA for the DB(W_b) specimen were generally less than for the $MC(W_b)$ specimen for each test condition. The difference in K values at test termination may be attributed to the fact that crack arrest was not achieved and that the rate of stress intensity decay varies with crack growth for the two specimen configurations. Selective comparisons in the figure allow evaluation of the remaining test variables. Comparison of appropriate test conditions indicates that K_{If} values were consistently greater for specimens exposed at $K_{\rm H}$ than for specimens exposed at $K_{\rm L}$.



FIG. 7—Load-deflection curves measured after exposure for specimens with various amounts of crack growth, Δa : (a) $MC(W_b)$ specimens and (b) $DB(W_b)$ specimens.

The effect observed is consistent for both specimen configurations and is due to the fact that crack arrest was not achieved in these tests. The method of precracking had no significant effect on $K_{\rm lf}$ in either the $MC(W_b)$ or $DB(W_b)$ specimen configurations. Further comparisons show that, as expected, there is no significant, reproducible difference in $K_{\rm lf}$ values due to surface grooving.

Final stress intensity values calculated by RBA and averaged for each test condition for data from the participating laboratories (interlaboratory variability) are shown in Table 3 along with the accompanying standard deviation. Comparing specimen configurations, the mean values were lower for the $DB(W_b)$ specimens in all but one test case. Standard deviation was greater in all cases but one for the $DB(W_b)$ than $MC(W_b)$ and were generally greater for the mechanical precrack and high starting stress intensity test conditions. This is a reflection of the greater variation in starting stress intensity levels caused by the large plastic



FIG. 8—Final stress intensity values for each factorial test condition shown as an average of data from all participating laboratories.

deformation introduced during mechanical precracking, and the greater compliance of the $DB(W_b)$ specimen, as well as difficulties with visual crack length measurements, and the fact that crack arrest was not achieved. The fracture surface irregularities noted for the mechanically precracked test cases also contributes to the preceding observations.

Statistical variations in final K values for each laboratory (intralaboratory variability) are shown in Table 4. Since starting stress intensity level and method of analysis were identified as significant sources of variability, the data presented is averaged for all other test variables. Data from some of the participating laboratories have noticeably greater standard deviations

		W_b)	DB(W_b)
Test Condition	\overline{X}	\$	\overline{X}	s
F-S-K ₁	9.22	2.26	9.30	2.50
$F-S-K_{H}$	11.34	2.38	9.58	3.10
$F-G-K_1$	8.66	2.58	8.12	2.21
$F - G - K_{H}$	11.07	2.54	9.68	3.80
$M-S-K_1$	9.70	1.19	8.83	3.18
M-S-K _H	11.63	1.72	8,96	3.53
$M-G-K_1$	9.84	2.19	8.22	3.89
$M-G-K_{H}$	12.30	4.26	10.73	4.64

TABLE 3—Mean (\overline{X}) and standard deviation (s) of final K values for each factorial test condition (S and G indicate smooth-faced and face grooved specimens; F and M indicate fatigue and mechanical precracking; and K_L and K_H indicate low and high starting stress intensity levels; respectively).

	Final	Load	Rigid	Bolt	
Laboratory		K _H	KL	K _H	
3	10.52	13.90	10.07	12.23	
	±1.56	±2.11	±1.85	±3.29	
4	7.96	10.17	7.45	8.82	
	1.33	4.19	1.35	2.63	
5			2.53 0.64	3.22 0.98	
8	4.75	6.09	6.63	4.44	
	1.05	4.67	3.16	1.26	
9	9.84	12.27	9.09	12.83	
	0.82	2.38	1.76	2.11	
10	10.18	14.14	9.98	12.67	
	0.57	2.17	0.67	2.18	
11			7.53 1.74	7.40 1.87	
13	9.61	10.83	6.74	7.06	
	2.81	4.74	2.60	1.99	
15	12.28	13.82	9.73	9.90	
	1.20	1.76	2.10	1.39	
16	10.00	12.79	7.05	8.02	
	2.05	3.45	1.18	1.55	
17	10.53	13.71	10.84	11.93	
	0.94	3.58	0.47	1.12	

TABLE 4—Mean and standard deviation (\pm) of final K values for each laboratory (K_L and K_H indicate low and high starting stress intensity, respectively).

than others, indicating some laboratories had more difficulty executing the complex test procedure. The variations in corrosion product accumulation noted earlier may also contribute to the large standard deviation variations. In all cases, the mean values were greater for specimens exposed at high K than those started at low K, but again this is due to crack arrest not occurring. The mean values were generally greater for data based on final load than for that calculated by RBA. The range of standard deviations was about 1.5 times greater for the data based on $P_{\rm f}$ than on RBA, and is an indication of the error inherent in the reloading technique.

Concluding Remarks

An interlaboratory program was conducted to evaluate the variability in determination of the stress corrosion threshold stress intensity factor (K_{ISCC}) and crack growth rates (da/dt) by using precracked specimens. Constant deflection, K-decreasing tests were conducted with commercially processed 7075-T651 plate in 3.5% NaCl with modified compact (MC(W_b)) and double beam (DB(W_b)) bolt-loaded specimens. Stress intensity solutions and compliance relationships were evaluated for both specimen configurations. The effect of specimen configuration, starting stress intensity level, precracking procedure, and surface grooving on stress corrosion data were evaluated and both interlaboratory and intralaboratory statistical variation presented. Stress intensity solutions developed by Newman and Fichter for the $MC(W_b)$ and $DB(W_b)$ specimen configurations agreed well with previously defined solutions, but the current solutions also allow for proportional scaleup of specimen dimensions. Additionally, Newman's solution accurately accounts for the loading geometry. Compliance relationships determined experimentally for both specimens compared well with other previously published solutions for the practical ranges of a/W and a/H. The relationships developed by Newman to correlate load-line displacement with crack-mouth opening displacement were found to be very accurate when compared to experimentally generated values.

Crack growth data indicated stress corrosion cracks grow in a noncontinuous manner, exhibiting several perturbations in crack length versus time curves, which may be due in part to difficulties with visual crack length measurements on the specimen surfaces. Data from miniature load cells indicated that the observed changes in crack velocity may be real and may represent accelerations due to corrosion product wedging. Determining final load by specimen reloading is experimentally difficult due to crack closure effects caused by corrosion product wedging and mismatch of delaminated crack faces, and closure effects are more significant for larger amounts of stress corrosion crack growth.

Results from the interlaboratory program indicate that both specimen configurations are suitable for stress corrosion evaluation of aluminum alloys and that differences in final stress intensity values were likely related to test procedures. Although final stress intensity values were slightly less for the DB(W_b) specimens than for the MC(W_b) specimens at test termination, the difference may be related to crack arrest not occurring during the exposure period. Neither the presence of face grooves nor the precracking method had any significant effect on final stress intensity test conditions. Starting stress intensity level had a significant effect on final K values, but again, this effect may be due to crack arrest not occurring. These observations indicate that test duration should be determined from analysis of crack growth data during the exposure period. The observed effects indicate that test duration appears to be a function of the crack growth behavior of the particular specimen configuration, the desired target arrest rate, and the resolution of the crack length measurement technique, and will not be a constant value regardless of these parameters. The data generated in both the interlaboratory program and the additional studies should provide adequate information for establishing a standard practice for using precracked specimens to evaluate stress corrosion susceptibility of aluminum alloys. While precracked specimens evaluated with fracture mechanics principles provide a method of quantifying SCC behavior, test parameters such as starting stress intensity level and test duration must be determined systematically. Finally, while the present study provides valuable information toward establishing a standard test method for measuring $K_{\rm ISCC}$ and da/dt, additional studies are necessary to resolve questions associated with analysis methods.

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Influence of Experimental Variables on the Measurement of Stress Corrosion Cracking Properties of High-Strength Steels

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ABSTRACT: A systematic investigation was undertaken to examine the influence of experimental variables on the measurement of stress corrosion cracking (SCC) properties of two high-strength steels using fracture mechanics test procedures. The properties of interest were the SCC threshold stress-intensity (K_{ISCC}) and time-based crack growth rate (da/dt). Two quench-and-tempered alloy steels in the form of rolled plate material were tested. The steel had yield strengths of 965 MPa (140 ksi) and 1207 MPa (175 ksi). The primary experimental variables investigated included: (1) specimen type (bolt-loaded wedge-opening loaded (WOL) and cantilever beam); (2) bulk solution chemistry (3.5% NaCl in distilled water and natural seawater); (3) dissolved oxygen content of the bulk solution; (4) electrode potential (open circuit and -1.0 V versus Ag/AgCl); (5) method of applying cathodic protection (potentiostat and zinc couple; (6) precracking stress-intensity level; (7) initial applied stress-intensity level; and (8) test duration. The effects of these experimental variables on K_{ISCC} and da/dt measurement are reported and the implications of these findings on test method development are discussed.

KEY WORDS: stress corrosion cracking, high-strength steels, steels, cantilever specimen, wedge-opening loaded specimen, cathodic protection, fatigue (materials), cracking, environmental effects

The propagation of cracks in high-strength steels is a potential problem for marine structures. One of the major contributing factors to this problem is crack growth induced by combined environment/static-load effects that is known as stress-corrosion cracking (SCC). While very few structures are statically loaded, and therefore the SCC properties of the materials cannot be used directly in design, the resistance of materials to SCC is an indicator of their performance measured by more complex, but realistic criteria. A great deal of research on the phenomenon of SCC and its implications for material selection and design of structures for use in the marine environment has been performed [1-11]; much of this information is contradictory, in part because experimental procedures have not been unified. Chemical interactions between environmental solutions and metals, particularly at the tips of deep, sharp cracks in test specimens, and mechanical driving force considerations are

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each complex, and the consequences of these combined factors are nearly impossible to predict or understand completely.

One way to alleviate some of the experimental problems is to conduct comparative studies of experimental variables to establish a consistent basis for evaluation of materials behavior. The most pressing issue for marine applications, in particular for high-strength steels, is one of specimen selection and test procedures. For steels, the choices are the cantilever beam (CB) [2] and the wedge-opening loaded (WOL) [3] methods. The principal difference between the two is the stress-intensity factor (K) gradient, that is, K-increasing in the CB method and K-decreasing in the WOL method, that results from geometric and loading conditions. In theory, the two should yield the same result when applied to the same material; in practice, differences have been large and comparisons between the two have been inconclusive. A significant amount of research directed toward evaluation of experimental methods for conducting the tests has been reported [4-12]; however, general agreement among investigators is still lacking. Questions of test duration, including initiation time, effects of test environments (3.5% NaCl versus natural seawater), effects of cathodic protection, adequacy of test specimen dimensions, and specimen preparation techniques are the subject of debates regarding the validity of test data. Such questions must be resolved before a standard method for conducting tests to determine the resistance of metallic materials to SCC can be introduced. Accordingly, a program to investigate the influence of some of these variables for steels of interest for marine applications has been conducted.

Experimental Approach

Two high-strength steels were chosen for evaluating the effects of experimental variables. These were a 5% Ni (nickel) steel with moderate sensitivity to SCC and 4340 steel at a strength level where a high degree of sensitivity to SCC is expected. The mechanical properties of these steels are shown in Table 1. The major issues to be addressed were (a) whether the CB or the WOL method is better for evaluation of the SCC resistance of steels and (b) the influence of geometric factors and test procedures on the results obtained from tests using each specimen type. The specimens are shown schematically in Fig. 1; all of the test specimens were nominally 25-mm thick. A set of parallel experiments involving identical environmental and electropotential conditions for each steel was planned in order to isolate differences in measured values that result from differences in specimen geometry and test procedure, if any. The variables examined included specimen precracking procedure and electropotential conditions of open circuit (OCE), coupled to zinc anodes (Zn) and potentiostated to -1.0 V versus Ag/AgCl.

The primary reasons for using the WOL specimen are that a value of $K_{\rm ISCC}$ can be determined from a single specimen and that this value is determined at the arrest condition, and thus does not depend strongly on the initial loading conditions. To conduct the test, a load sufficient to produce a K value well above the expected $K_{\rm ISCC}$ is applied using a bolt, so that

Material	Yield Strength, MPa	Ultimate Strength, MPa	Reduction in Area, %	Elongation, %	Fracture Toughness, MPa √m
5-Ni	965	1014			145
4340	1207	1282	25	11	91

TABLE 1-Mechanical properties of steels for SCC experiments.



FIG. 1—Configurations of specimens used for comparisons of test methods. At top is the 1T WOL specimen and at bottom is the cantilever bend specimen.

the load-line displacement is constant. The crack is allowed to grow until arrest, which occurs because K decreases with increasing crack length. The WOL specimens were fatigue cracked at different loads to different precrack lengths; these factors were a variable in the program.

To get the maximum amount of data for the least manpower, a computer data acquisition system was devised for tests using WOL specimens [13]. A system of inexpensive power supplies and signal conditioning modules was assembled to monitor the signals from straingaged loading bolts; the system was connected to a personal computer. Software to monitor the signals, to compute load, crack-length, and K from the input, and to record these data, as well as elapsed time, was written. Standard [14] K and crack length compliance expressions for WOL specimens were used for the computations. The data to be recorded were selected on the basis of minimum increments of crack length, K, and elapsed time, which were input values to the program; this was necessary to prevent the accumulation of masses of unusable data. Test cells were plexiglass boxes that contained approximately 1.6×10^{-3} m³ of solution; each specimen was tested in a single cell. The solution for all of the tests conducted with WOL specimens was 3.5% by weight NaCl in distilled water; the solution was changed weekly, with evaporation losses being made up daily with distilled water. Tests were conducted in a laboratory where the temperature was controlled at 24°C. Effects of such variables as dissolved oxygen content, contaminants, etc., were not investigated using WOL specimens. It was assumed that their effects were a constant, probably second order, and would not influence the comparisons to be made in this investigation. Zinc anodes with roughly the same wetted area as the specimen and inexpensive electropotentiostats were connected to the specimens to be tested under those conditions. Optical monitoring of the crack length during the test was not necessary.

Initial loading was accomplished using the procedures of Ref 3. A clip gage (strain-gaged beam-type displacement gage), having a sensitivity of $\pm 10^{-1}$ mm, was used to monitor crack-mouth opening (CMO) during the initial loading; this gage was removed when the desired test load was reached. At the conclusion of the test, the clip gage was reinstalled and the CMO was recorded. The loading bolt was removed, the specimen was placed in a tension test machine, and the load required to reopen the specimen to the final CMO value was recorded, without removing the clip gage; the load measured in this way was used to compute the value of K_{ISCC} for each specimen. This procedure alleviated the need to allow for the effects of corrosion product wedging to cause continued crack growth after removal of the bolt, since a very short time elapsed between bolt removal and final load determination. Following this, the specimen was fatigued to mark the final crack length and to expose the fracture surfaces. Final crack lengths were measured at eleven equally spaced points across the thickness, including the outer edges, which were averaged to count as one value. Using the final load measured in the tension test machine and the measured final crack length, a value of K_{ISCC} was computed for each specimen.

As shown in Fig. 1, CB test specimens are single-edge-notched specimens that are tested by clamping one end and loading with dead weights suspended from an extension arm. Since the loading moment is constant, any extension of the crack results in an increase in K; the compliance of the specimen is such that K increases very rapidly with crack growth. The test method is to vary the initial $K(K_0)$ by loading a series of specimens at K_0 levels above and below the expected K_{ISCC} value. Time to specimen failure is recorded and the data are usually displayed on a plot of K_0 versus time. Bracketing methods are used with specimens that fail due to SCC and specimens that do not fail in a set time increment to determine the K_{ISCC} value. In this work, the K_{ISCC} value was taken as the highest K which was sustained for the set test duration without failure. The test duration varies with the material being evaluated and is the subject of much controversy. The arbitrarily defined test time for this work was 1000 h for the 4340 specimens and 10 000 h minimum for the 5-Ni steel specimens; most specimens were removed from test if no crack growth was evident after this elapsed time.

All of the CB specimens were fatigue precracked; as with the WOL specimens, precracking loads were varied to determine the effect of this practice. The specimens were tested in load frames designed for this purpose; the test cells were polyurethane containers cemented around the test section of the specimen and the test solutions were the same as used for WOL specimens. While there has been no K calibration published specifically for cantilever loading, the expressions by Kies et al. [15] and by Tada [16] for edge-notched beams were considered adequate and were used to compute the K values.

Results and Discussion

The values of K_{ISCC} measured by both methods were in remarkably good agreement for 4340 steel and in reasonable agreement for 5-Ni steel; the final values are given in Table 2.

		$K_{\rm ISCC}, N$	$\frac{1}{1}$ IPa \sqrt{m}	
		5-Ni	4	340
Condition	СВ	WOL	СВ	WOL
OCE Zinc -1.0 V	 115 94	 86 	33 23 20	35 21 22

TABLE 2—Values of K_{ISCC} for two steels measured by different test methods.

The apparent discrepancy of 115 MPa \sqrt{m} (CB) versus 86 MPa \sqrt{m} (WOL) for 5-Ni steel coupled to zinc reflects experimental difficulties rather than a real difference between the test methods. The values for test conditions of zinc-coupled and -1.0 V potential should be grouped for purposes of comparison of the method. Experimental difficulties were encountered in tests with the WOL specimen when potentiostated to -1.0 V; the difficulties were in the potentiostats, which allowed excursions of the voltage to higher values, thereby producing hydrogen and very rapid crack growth. For the WOL specimens, coupling to zinc was a much more reliable method to attain the desired voltage. In the CB specimens, it was observed that the deposits of zinc oxide on the specimen and particularly in the open crack probably interferred with the access of the solution to the crack tip and caused an elevation of the observed $K_{\rm ISCC}$. Such deposits were also noticed on the WOL specimens, but since the initial value of K (K_0) was high compared to $K_{\rm ISCC}$, the effect was negligible. In the CB specimens, the K_0 values were close to the final K_{ISCC} value and the initiation times were long, so that the presence of the oxide was significant. Comparing the value recorded at -1.0 V potential with CB specimens with the value recorded under zinc-coupled conditions with WOL specimens gives satisfactory agreement for tests of this type. It is noted that crack growth due to SCC was not observed in the 5-Ni steel under open circuit potential conditions. Further, the experimental difficulties encountered were faults in the ancillary equipment rather than being inherent to the test method or test specimen configuration; these faults appeared after long test times had elapsed and illustrate the difficulties associated with using electronic equipment in a harsh operating environment for long-term experiments. The total test times were very long in the 5-Ni steel for both specimen types, and were longer in the WOL specimen than in the CB specimen. Test times in 4340 steel were much shorter than test times in 5-Ni steel for both specimen types; hence there was better agreement in results for 4340 than for 5-Ni steel.

The most important difference in the results obtained comparing the test methods was in the initiation time, that is, the time from the loading of the test specimen until crack growth began. Fatigue precracking practice had a strong effect on initiation time for the 4340 steel. To evaluate this factor, one set of specimens of both types was fatigue precracked at an applied K (K_f) of 50 MPa \sqrt{m} and another set was precracked at a K_f less than 25 MPa \sqrt{m} . Initiation time for the WOL specimens is plotted as a function of the ratio of applied initial loading to K_f in Fig. 2; in this figure, the data for $K_f < 25$ MPa \sqrt{m} include data for specimens initially precracked at the high K_f and later cracked further by load shedding techniques to reduce the final K_f . Clearly there is a great advantage in causing crack growth to begin as soon as possible in experiments of this type. Reductions in initiation time from the order of months to the order of hours can be attained by setting the precracking loads to approximately half of the expected K_0 value or less. Similar results were seen in comparisons of the values obtained from CB specimens, Fig. 3. In the CB specimens, the



FIG. 2—Time for initiation of crack growth depends on the ratio of $K_{initial}/K_{faigue}$ (K_o/K_f) for tests using WOL specimens.

reduction in initiation time is inferred from the reduction in total time for specimen failure at a given K_0 ; on the plot the apparent reduction in K_{ISCC} at the lower K_0 value is due to initiation effects. It is assumed that the runout data points for specimens precracked at the higher K would fail due to SCC if left on test long enough; however, for practical reasons the result is that erroneously high values of K_{ISCC} can be measured under these conditions. This figure is very strong evidence that precracking loads should be minimized for SCC tests.

Initiation effects were also observed in 4340 steel as a function of initial loading relative to K_{ISCC} and whether cathodic coupling was present. In the CB specimens, initiation time does not depend strongly on initial loading. Since the curves in Fig. 3 tend to be rather steep in the region where specimen failures took place, it is assumed that initiation time is short and most of the time is taken by the crack growth phase. Initiation time can be reduced in WOL specimens by loading at higher K_0 values, Fig. 4; however, the risk in this practice is that the crack growth necessary to reduce K_0 to K_{ISCC} will be very large and the data will be suspect, as will be discussed. As shown in Fig. 4 from the coding of the symbols, there is a weak tendency for those specimens coupled to zinc or potentiostated to -1.0 V versus Ag/AgCl to initiate crack growth more quickly than those tested in the open circuit condition, at the same value of K_0/K_{ISCC} . The initiation times for the WOL specimens were on the same order as total test times for CB specimens for experiments with 4340 steel.



FIG. 3—Strong effect of precracking K on the apparent K_{ISCC} is shown for tests with cantilever bend specimens. It is assumed that specimens precracked at high loads would fail if tested for sufficient times.

Comparisons of test results pertaining to initiation time in 5-Ni steel yielded entirely different results than were observed in 4340 steel. In 5-Ni steel, KISCC was much higher than any normally used precracking load so that this was not a factor. Cracks would not grow in 5-Ni steel under open circuit potential conditions in either specimen type. Data for both specimen types are plotted in Fig. 5, on the premise that, at the long initiation times shown, most of the time for CB specimens to fail is taken up in the crack initiation phase. Two things are obvious from the figure; first, there is roughly an order of magnitude difference in initiation time between WOL specimens and CB specimens and, second, to get cracks to grow in WOL specimens of this material, the K_0 must be very high. If one considers that $K_{\rm ISCC}$ for this alloy is approximately 90 MPa \sqrt{m} , a high degree of crack-tip plasticity is introduced into the specimen to attain $K_0/K_{\rm ISCC} = 1.5$ or greater, as is indicated in Fig. 5. Since this was done for the experiments with 5-Ni steel, the values of K_0 reported may not represent linear elastic conditions. However, the invalidity of the initial loading conditions does not render the test invalid, since the K values diminished to levels that are predominately plane-strain at the time of crack arrest. To reach the plane strain state, crack growth well in excess of the induced plastic damage zone was necessary. Thus, it is necessary to load the WOL specimens to indicated K_0 values to initiate crack growth in these specimens. The probable cause for such behavior, aside from crack tip chemistry effects, is the tendency of the loading system to permit relaxation of the loading fixtures and plastic flow at loading points; these events reduce the applied K at the beginning of the test, leaving a residual plastically deformed region at the crack tip. Reductions of 3 to 5% of the initial K values were observed in specimens of both steels, even where no crack growth took place. This



FIG. 4—Initiation time can be reduced in WOL specimens by increasing the initial K relative to K_{ISCC} . A weak effect of electrochemical potential to reduce initiation time is also observed.

does not happen with the CB specimens; hence, the large difference in initiation times between the two specimen types.

An additional factor not often considered in using the WOL specimen is the limitation that should be applied to the value of crack length at crack arrest, where K_{ISCC} is computed. Difficulties result mainly from the variability that occurs when the cracks are too long; the scatter comes from the high sensitivity of the K calibrations to small errors in either measured load or crack length when the crack becomes very long. Figure 6 illustrates this point by a plot of the three published K calibrations [11,12,14] versus normalized crack length. In the range where all three are valid, there is little difference to be found; however, outside their respective valid ranges, they diverge significantly. It is tempting to use the expression for pin loading since the range of validity is 0.2 < A/W < 1.0. The steepness of the curve in



FIG. 5—In 5-Ni steel, initiation time for WOL specimens is in excess of an order of magnitude compared to initiation time for CB specimens. It is also apparent that loading well in excess of K_{ISCC} is necessary to cause crack growth in WOL specimens.

the region above A/W = 0.8 renders computed K values subject to small errors in determining final crack length (the final crack front is often very irregular); the magnitude of the values of K/P, where P = applied load, makes the computed K subject to errors in load measurement (loads are usually quite small at the end of the experiments). Data to illustrate the preceding points are contained in Fig. 7, which shows the variation that can occur at long crack lengths, compared to the small scatter at short crack lengths.

A significant amount of variation was observed in computed crack growth rates (da/dt) for both steels measured using WOL specimens. These data are not shown, but it is considered that the scatter results from both the variation of local metallurgical conditions to be found in all metals and the unreliability of the experimental equipment. The use of straingage devices and associated measurement and recording devices in an atmosphere containing salt and chlorine for long test periods requires a great deal of maintenance to assure reliable results. Additionally, there are sources of error in calibrating bolts and in loading specimens that were shown to exist. Comparisons of K values computed by various means showed that the initial K computed from loads indicated by strain-gaged bolts may be in error up to 20%; these errors are expected to carry over into the crack growth phase of the test. For this reason, these values must be taken as estimates and the data interpreted with cognizance



FIG. 6—Variation of K/P as a function of normalized crack length (A/W) given by three different K calibration expressions. Novak's equation applies in the range 0.3 < A/W < 0.75, the LeFort and Mowbray expression applies in the range 0.2 < A/W < 0.8 and the pin-loaded expression applies in the range 0.2 < A/W < 1.0.



FIG. 7—Wide data scatter at A/W > 0.8 for both steels tested using WOL specimens is strong evidence that this crack length should be a limiting value for determining K_{ISCC} .

of possible errors. It may also be considered that da/dt may not be a bulk property of steels, or other metals for that matter, and such variations should be expected.

Parallel experiments using cantilever bend specimens of the 5-Ni steel were conducted at the LaQue Center for Corrosion Technology [17] in a flowing natural seawater environment. In these experiments, the natural seawater solution was circulated over the specimen and was then drained. A comparison of these results with similar results obtained in a 3.5% NaCl solution is shown in Fig. 8; the major difference is in initiation time. There are not sufficient data to make good comparisons of $K_{\rm ISCC}$; however, the data do show that specimen failure takes place at much shorter times in 3.5% NaCl solution than in seawater at the same values of K_0 . Large differences in $K_{\rm ISCC}$ are not expected as a result of these different aqueous environments. While these comparisons are not based on rigorous analyses of environmental composition, they do illustrate that there is a great advantage to reducing initiation time through the use of synthetic environments to simulate seawater, and the 3.5% NaCl solution appears to do this quite well.

There were several ancillary observations made during the experiments that are germane for development of standard methods of test for resistance of metallic materials to SCC:

- 1. The dissolved oxygen content in the aqueous solution used for these experiments had no discernible effect on the results, either in initiation time or in K_{ISCC} values determined in CB tests. This means that it is not necessary to circulate the solution during experiments; a quiescent solution is adequate.
- 2. It was confirmed experimentally that, in WOL specimens, the load should not be reduced once it is applied. This practice leads to extremely long initiation times, if not to complete prevention of crack initiation.





FIG. 8—Comparison of results of tests with cantilever bend specimens in natural seawater and in the 3.5% NaC laboratory solution. While there is no apparent effect on K_{ISCC} , initiation times are an order of magnitude shorter in the laboratory solution.

3. A source of much difficulty in tests of 4340 steel using WOL specimens was the tendency of the crack to grow out of plane, despite the use of sidegrooves. This renders the test results invalid except for determination of initiation time. A related difficulty was the irregularity of crack fronts at final arrest.

Summary and Conclusions

In this program, an attempt was made to investigate aspects of SCC testing that pertain to experimental methods or techniques, rather than on mechanisms of crack growth or interpretations of data to use of materials. The most important findings are listed here.

- 1. The question of whether to use bolt-loaded WOL specimens or CB specimens to evaluate a particular material must be answered in terms of whether the material is expected to be highly sensitive or nearly insensitive to SCC, and the information that is needed from the test. Neither method is as simple or straightforward as it may seem from a reading of the literature. Either method works reasonably well for highly sensitive steels. The WOL method has the advantage that crack growth rates can be determined, if needed; this is difficult when using the CB method. For steels where the resistance to SCC is high and the initiation times are long, the CB method is preferred because of the directness of the method. The long initiation times cause problems with monitoring equipment used with WOL specimens; use of manual methods to monitor crack growth in WOL specimens is so labor intensive that extensive use of the method is unlikely. An additional factor against the WOL specimen for measuring SCC properties of steels with high resistance to SCC as well as high fracture resistance, is the necessity to begin with specimens loaded well outside the boundaries of linear elastic fracture mechanics. The only alternative method to overcome these conditions is the use of very large specimens to increase constraint to plastic flow; this, however, defeats the purpose of SCC testing with specimens of this type.
- 2. Fatigue precracking of specimens requires a great deal of attention to ensure that the test results are not influenced by residual plastic regions, particularly for steels with low resistance to SCC and even more so for CB specimens of such materials. Good rules to follow for precracking are that the final K_f should be less than half of K_{ISCC} for CB specimens and less than half of K_0 for WOL specimens. Load shedding techniques for precracking were found to be acceptable.
- 3. When tests are to be conducted under conditions of applied potential, either potentiostats or sacrifical anodes can be used. Both present problems. Anodes, such as zinc and aluminum, precipitate hydrated oxide particles into the test solution and form protective coatings so that they must be cleaned periodically. If the anodes are not cleaned often, the potential is reduced. Systems using electro-potentiostats are subject to corrosion at the contact points and at electrical connections, which cause them to malfunction. Regular monitoring of these devices and periodic maintenance is also necessary. The major problem is that malfunction of these devices often causes the potential to increase, resulting in the production of hydrogen in the specimen and causing rapid crack extension. It is believed by the authors that this problem is often undetected.
- 4. The subject of test time for either specimen type is determined by the initiation time in both, provided proper fatigue precracking techniques are employed, since the event of crack growth is obvious once it begins. Though it is not apparent from the experimental data, the nominal values of 1000 h for steels sensitive to SCC and 10 000 hours for moderately sensitive steels are good rules of thumb. Longer test time requirements

make the test impractical to use on a large scale; shorter test time requirements make the data suspect. In the CB tests of 5-Ni steel potentiostated to -1.0 V, there were no failures of specimens in the 3.5% NaCl solution after 266 h; there was a failure of a specimen coupled to zinc at 6700 h.

- 5. The comparison of data for samples tested in laboratory solutions versus natural seawater indicated that the use of the laboratory solution resulted in a lower initiation time, with no obvious effect on $K_{\rm ISCC}$. This result indicates that the laboratory solution is an acceptable substitute for natural seawater in SCC tests; differences in test results are probably smaller than the acceptable error.
- 6. Maintenance of electronic equipment used to control test conditions and to monitor the tests and assurance that the information derived from such devices is accurate should be accorded a high priority in conducting SCC tests by either method. Malfunction of electronic gear can lead to erroneous results that may never be detected.

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Material Performance—III

Keyhole Compact Tension Specimen Fatigue of Selected High-Strength Steels in Seawater

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ABSTRACT: Fatigue experiments have been performed in flowing natural seawater on nine different steels with yield stress in the range 370 to 990 MPa (54 to 143 ksi) employing keyhole compact tension specimens. All experiments were at a frequency of 1.0 Hz and R = 0.5. Corrosion state was either freely corroding (FC) or cathodically polarized (CP) to -1.10 V saturated calomel electrode (SCE). Limited experiments were also performed in air. Seven of the steels represent relatively new technology where strengthening involves either (1) precipitation hardening, (2) microalloying and quenching and tempering, (3) control rolling, or (4) thermomechanical control processing (TMCP). The results are represented in a $\Delta K(\rho)^{-1/2}$ versus cycles to initiation format and are evaluated with regard to the effects of environment and cathodic polarization. Endurance limit (CP tests only) was related to tensile strength and fracture behavior.

KEY WORDS: corrosion fatigue, cathodic polarization, crack initiation, endurance limit, fracture, high-strength low-alloy steels, keyhole compact tension specimen, seawater, fatigue (materials), cracking, environmental effects

Nomenclature

- a Keyhole notch length
- **B** Specimen thickness
- CP Cathodically polarized
- EL Endurance limit (expressed as range)
- FC Free corrosion
- $K_{\rm t}$ Stress concentration factor
- **R** Ratio of minimum to maximum stress (or stress intensity)
- W Specimen height below the line of loading
- ΔK Stress intensity range
- $\Delta \sigma$ Applied stress range
- σ_y Yield strength
- σ_{T} Tensile strength
- p Keyhole root radius
- φ Electrochemical potential

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Innovative structural concepts for deep-water petroleum production platforms require steels of higher strength (400 to 800 MPa yield) than have historically been employed [I]. While the high yield (HY) class of steels possesses high strength and excellent toughness and, consequently, has been employed for several decades as a submarine hull material [2], emphasis is also being placed upon relatively new alternatives with reduced alloy content and improved weldability. Of particular concern with regard to offshore structural applications is loss of ductility and susceptibility of higher strength steels to brittle fracture as a consequence of cathodic polarization.

The fatigue process is generally represented in terms of a crack initiation stage followed by crack propagation to a critical size. Offshore applications have historically involved aswelded connections in which case the crack initiation process has been projected as minimal compared to propagation [3]. However, welded high-strength steels are likely to be employed in the ground and post-weld heat treated condition and also as threaded connections, in which cases crack initiation may become the critical parameter influencing system integrity. Corrosion fatigue crack initiation has been reviewed by several authors [4,5], and while some understanding of this process has evolved for the freely corroding case, only limited experiments have been performed that address the effects of cathodic polarization [6-9]. Of particular concern here is the relatively recent development of new steels that are strengthened by precipitation hardening, microalloying, control rolling, and thermomechanical control processing. The purpose of the present study was to investigate the fatigue properties of exemplary alloys as applicable to marine applications.

Experimental Procedure

Materials

Nine steels were employed in the test program, and are listed along with their chemical compositions in Table 1. It was intended that these represent examples of the best material available at the respective strength levels or for the particular type of processing, which included (a) precipitation hardened (A710), (b) microalloyed quenched and tempered (QT80 and QT108), (c) thermomechanical control processed (A537 a.c. and d.q.), and (d) control rolled (EH36 and X70). HY80 and HY130 were studied primarily for comparison purposes, since these have been investigated in numerous prior programs [10]. The yield and tensile strength properties of the steels are listed in Table 2.

Specimens

Keyhole compact tension specimens 25.4 mm thick, of the LT orientation and conforming to ASTM Test Method for Constant-Load-Amplitude Fatigue Crack Growth Rates Above 10^{-8} m/Cycle (E 647-83) [11] were machined according to the geometry in Fig. 1. Previous investigators have demonstrated that this specimen type provides a geometry-insensitive approach to initiation studies [12,13] when stress state is expressed as $\Delta K(\rho)^{-1/2}$, where ΔK is the stress intensity range and ρ is the notch root radius. Thus, finite-element analysis has shown that the fracture mechanics representation applies for a wide range of ρ values [12]; and this has been confirmed experimentally as well [14]. Initiation for the present study was defined as having occurred when a 1-mm-long crack had propagated from the notch root on both surfaces of the specimen. However, since the stress intensity factor was high at the crack tip and the test was conducted in load mode, relatively few additional cycles were required for complete fracture. Thus, the specimen was relatively insensitive to the definition of crack initiation.

	Steel									
Element	HY80	A710	QT80	QT108	EH36	A537 d.q.	A537 a.c.	X70	HY130	
С	0.13	0.04	0.08	0.11	0.13	0.12	0.07	0.09	0.10	
Si	0.16	0.30	0.23	0.23	0.37	0.41	0.26	0.41	0.14	
Mn	0.28	0.45	1.40	0.86	1.42	1.30	1.35	1.43	0.80	
Р	0.005	0.004	0.01	0.004	0.018	0.014	0.011	0.018	0.006	
S	0.005	0.002	0.002	0.003	0.002	0.003	0.003	0.002	0.005	
Cu	0.02	1.14	0.01	0.24	0.01	0.01	0.14	0.01	0.12	
Ni	3.08	0.82	0.43	0.98	0.01	0.03	0.14	0.01	5.09	
Cr	1.70	0.67	0.09	0.43	0.02	0.04	0.01	0.02	0.46	
Mo	0.44	0.18	0.06	0.44	0.01	0.05	0.02	0.10	0.51	
Nb		0.037	0.002		0.025		0.017	0.032		
V	0.006	0.004	0.04	0.027	0.003	0.044		0.063	0.062	
В	0.0001	0.0001	0.0001	0.0009						
Ti	0.004	0.002	0.005		0.022			0.018	0.008	
Ν	0.0089	0.0047	0.0026		0.0038		•••	0.0026	0.01	
Sol. Al	0.019	0.034	0.051		0.046			0.026	0.021	
0	0.0031						•••		0.0012	
Carbon										
equivalent	0.7108ª	0.4165^{b}	0.3807*	0.4853ª	0.3890ª	0.3781ª	0.3163ª	0.3700*		

TABLE 1—Chemical composition of test steels.

 b Ceq = C + Mn/6 + Cu/15 + Ni/15 + Cr/5 + Mo/5 + V/5.

	Yield Strength, MPa (ksi), Base Material (as-received)					Tensile Strength, MPa (ksi), Base Material (as-received)				
Steel	 L*	С	L	T	Z		С	L	Т	Z
HY80	636 (92.2)	654.6 (94.9)				736.5 (106.8)	742.9 (107.7)			
A710			563 (81.7)	563 (81.7)		•••		622 (90.3)	621 (90.2)	623 (90.5)
QT80	•••		537 (77.9)	533 (77.4)				613 (88.9)	611 (88.6)	610 (88.4)
QT108		74	45 (108)			824 (119)				
EH36	370.7 (53.8)	416.3 (60.4)				518.8 (75.2)	536 (77.7)			
A537 d.q.		50	00 (72.5)				5	98 (86.7)		
A537 a.c.		45	52 (65.9)				5	51 (80.3)		
X70	•••		509 (73.8)	534 (77.5)	••••		•••	•••	612 (88.8)	613 (88.9)
HY130		9	85 (143)				10	006 (146)		

TABLE 2—Material properties of the test steels.

NOTE-L = ladle, C = check, L = longitudinal, T = transverse, Z = through thickness direction.



FIG. 1-Schematic representation of KCT specimen.

Although it has been projected that crack initiation in KCT specimens is insensitive to surface preparation [13], particular care was given to this in the present case. Thus, the keyhole region was honed and subsequently polished in the circumferential orientation to a 600-grit finish. Final external surface preparation involved sand blasting and degreasing. Stress intensity for each specimen was calculated from the expression [15]

$$\frac{\Delta K}{\sqrt{\rho}} = \frac{\Delta P(W+a)}{2.B.\sqrt{\rho}(W-a)^{3/2}} \left[7 - 7.05(a/W) + 4.275(a/W)^2\right]$$
(1)

Test System

The fatigue experiments were conducted using a specially configured, eight-station load frame that employed a 98 kN (22 kip) MTS actuator, load cell, and a servo-hydraulic control system, as shown in Fig. 2. Since the specimens were in series, the test frame was operated in load control, but the interlocks were set so that the system would shut down if stroke exceeded an upper limit slightly greater than for normal operation. The technique was



FIG. 2-Custom configured eight-station load frame.

sufficiently sensitive that the interlock often engaged once a crack formed within the keyhole and prior to emergence to a side face. Load ratio, R, was 0.5 and frequency was 1.0 Hz for all tests. An open-to-atmosphere Plexiglas³ bath, as shown in Fig. 3, was mounted about each specimen for seawater containment. The seawater feed tank was replenished twice weekly from the Florida Atlantic University (FAU) Marine Materials and Corrosion Laboratory, which is located on the Atlantic Ocean in Boca Raton. Properties for this seawater during an annual cycle have been previously reported [8]. The flow rate through the bath was approximately 1 L per day. Besides an inlet and outlet, each bath had a salt bridge connection to a saturated calomel reference electrode.

Experiments were performed either freely corroding or cathodically polarized to -1.10 V saturated calomel electrode (SCE). This relatively negative potential in the latter case was intended to represent excessive cathodic protection and thereby reveal any embrittlement tendency of the steels. Polarization was effected by locally fabricated potentiostats based upon the circuit proposed by Baboian [16] and operating in conjunction with platinum coated niobium counter electrodes (see Fig. 3).

Once cracking had occurred to beyond the initiation limit, the bath was drained and the specimen washed with distilled water and dried with alcohol. The specimen was then removed and the keyhole portion sectioned and vacuum-stored for subsequent fractographic examination. The testing of remaining specimens was resumed after mounting either a new or dummy specimen upon the frame.

For Steels A710 and QT108, limited air tests (relative humidity 45 to 60%) were carried out for comparison purposes.

³ Registered trademark of Rohm and Haas Co.



FIG. 3-Seawater containment system for KCT specimen.

Results and Discussions

Fatigue data for each steel are represented in the form of S-N curves in Figs. 4 through 12 (where $S = \Delta K / \sqrt{\rho}$). Figure 13 summarizes on a single plot all the freely corroding data from these figures and illustrates that these conform to a common band, irrespective of composition and microstructure. For this test condition, corrosion potential was typically in the range -0.60 to -0.65 V, SCE. These S-N data are consistent with historically reported findings regarding corrosion fatigue strength [10, 17]. This suggests a common mechanism for fatigue crack initiation such as pitting-induced crack formation or enhanced corrosion at extrusions and intrusions [18]. Figure 14 presents a composite plot of all cathodically polarized data from Figs. 4 through 12. In contrast to the freely corroding results, this data exhibited run-outs indicating an endurance limit. As a general rule, more scatter was apparent for the cathodically polarized data than for the freely corroding. Table 3 illustrates this statistically, where the average correlation coefficient for the FC data was calculated as 0.981 and for the CP data as 0.835. In order to determine if the scatter reflected true material behavior or if it was due to different conditions for different test series, a set of experiments was performed involving concurrent testing of six specimens each of A710 and QT108. Special care was taken in the preparation to ensure uniformity for the notch surfaces. Table 4 presents the results for these tests and shows that the same level of scatter persisted as for the other results. On the other hand, air tests conducted on the same steels revealed relatively little scatter, as seen from Figs. 15 and 16. This suggests that a unique mechanistic feature or rate controlling step is associated with the CP crack initiation process compared to either air or FC.



FIG. 4—S-N plots for HY80.



Cycles to Initiation FIG. 5-S-N plots for A710.



FIG. 6-S-N plots for QT80.



Cycles to Initiation FIG. 7—S-N plots for QT108.



FIG. 8—S-N plots for EH36.



Cycles to Initiation FIG. 9-S-N plots for A537 d.q.



FIG. 10—S-N plots for A537 a.c.



Cycles to Initiation FIG. 11-S-N plots for X70.



FIG. 12—S-N plot for HY130.



Cycles to Initiation FIG. 13—Combined S-N plot for all steels—FC tests.




Endurance limits for the present CP experiments (horizontal dotted lines in Figs. 4 through 12) were correlated with tensile strength of the specific steels. This was done in terms of stress range, $\Delta\sigma$, according to the relationship [19]

$$\Delta \sigma = 2\Delta K(\pi \rho)^{-1/2} \tag{2}$$

Figure 17 illustrates this and shows that endurance limit was proportional to tensile strength up to approximately 680 MPa and was independent of tensile strength beyond this.

Based upon the data of Barsom and McNicol [20] and Clark [21], Roberts et al. [22]

	FC Te	sts	CP Tests		
Steel	Number of Data Points	Correlation Coefficient	Number of Data Points	Correlation Coefficient	
HY80	4	- 0.980	4	-0.935	
A710	5	-0.994	11	-0.589	
QT80	5	-0.998	8	-0.932	
OT108	4	~0.900	17	-0.730	
EH36	4	-0.997	11	-0.936	
A537 d.g.	4	-0.988	9	-0.775	
A537 a.c.	4	-0.999	8	-0.830	
X70	4	~ 0.992	8	-0.847	
HY130			4	-0.945	
Average		-0.981		-0.835	

TABLE 3-Statistics for FC and CP data.

Stress Ran	ge $\Delta K/\sqrt{\rho}$	Cuoles to	
ksi	MPa	Initiation	
74.75	515.34	214 020	
74.46	513.34	284 290	
74.08	510.77	332 320	
74.18	511.46	357 000	
74.34	512.56	430 000	
74.21	511.66	507 000	
	OT108		
69.01	475.81	228 180	
68.97	475.53	485 670	
68.94	475.33	595 210	
68.67	473.47	>2 364 200	
69.12	476.57	>2 364 200	
69.40	478.50	>2 364 200	

TABLE 4--Results for six specimens of two steels tested concurrently under identical conditions.

determined that endurance limit for notched specimens $(K_t \sim 2.5)$ fatigued in air with -1.0 < R < 0.5 conform to the relationship

$$\Delta K(\rho)^{-1/2} = 10(\sigma_{\rm y})^{1/2} \tag{3}$$

where σ_y is the yield strength of the material. For the same data [4,19], Rolfe and Barsom [14] proposed a correlation of the form

$$\Delta K(\rho)^{-1/2} = 5(\sigma_{\rm y})^{2/3} \tag{4}$$



Cycles to Initiation FIG. 15—The FC, CP, and air S-N plots for Steel A710.



Cycles to Initiation FIG. 16—The FC, CP, and air S-N plots for Steel QT108.



Tensile Strength (MPa) FIG. 17––Endurance limit versus tensile strength plot.



FIG. 18—Comparison of present CP data with air data of Roberts et al. [21] according to Rolfe et al. [14].

Figure 18 shows the data according to this representation and in comparison to the present CP results. When tensile strength was used to compare the endurance limit for different steels, the same data conformed to the expression

$$\Delta K(\rho)^{-1/2} = 0.9\sigma_{\rm T} \tag{5}$$

This, along with the present data, is shown in Fig. 19. Rolfe et al. [14] attributed the fact that both yield and tensile stress provide similar correlation with the threshold value for $\Delta K(\rho)^{-1/2}$ to the finding that the σ_y/σ_T ratio was within the range of 0.8 to 1.0 for the steels that they considered. The steels in the present program conformed to the same range (see Table 2).

Two points of importance are apparent by comparing the air and CP data in Fig. 19. First, the transition from a tensile strength dependent to independent endurance limit occurred in the former case (air data) at $\sigma_T \approx 1030$ MPa. This trend conforms to what has been observed historically for high-strength steels where moderation of the generalized relationship [23]

$$EL = \sigma_{T} \tag{6}$$



FIG. 19—Comparison of present CP data with air data of Roberts et al. [21] on a tensile strength basis.

is encountered. That the data in Fig. 19 show this to occur at relatively low σ_T may reflect the fact that a notched specimen was employed. For the CP results, the transition occurred at a tensile strength approximately 25% below the value in air. Second, in the endurance limit sensitive range, the CP data lie at a value approximately 18% below the air values of Roberts et al. [22]. Interestingly, this endurance limit reduction was constant over the applicable tensile strength range (370 to 680 MPa). However, comparison of the air and -1.10 V data in Figs. 15 and 16 suggests that for the present experiments, any difference between the two may be less than 18%.

Figure 17 revealed that all steels conformed to a common endurance limit versus tensile strength trend except QT108 for which EL was low by approximately 15%. In an attempt to explain this, scanning electron microscopy was performed upon fracture surfaces of both air and -1.10 V specimens. Thus, Fig. 20*a* illustrates the typical appearance for the former case (air tests) and shows this to be predominantly quasi-cleavage with local areas of intergranular separation, apparently along prior austenitic grain boundaries. Figure 20*b* shows the fracture surface morphology for the CP condition, where the amount of intergranular

cracking is greater than for air. By way of contrast, the other steels exhibited a quasicleavage fracture surface morphology not unlike the QT108 air test case.

A possible contributing factor to the relatively brittle fracture of QT108 may have been inclusion debonding [24], an example of which is presented in Fig. 21. Such features were more apparent compared either to QT108 fatigued in air or the other steels at -1.10 V. Alternately, it is feasible that this type of separation was due to some yet undisclosed prior austenitic grain boundary feature. Fatigue crack initiation by inclusion debonding typically occurs in steels of high strength [24], but it may be that the combined effect of notch geometry and polarization to -1.10 V permitted this process to trigger local intergranular separation in the present alloy. If such a mechanism is involved, it may be responsible for the data scatter (see Fig. 14 and Table 3) in which case the critical initiation event is a function of inclusion type, size, shape, and distribution in the notch root vicinity and how these features interact with cathodic reaction generated hydrogen.

Alternately, it has been reported that fatigue cracks preferentially initiate along prior austenitic grain boundaries for low-carbon martensitic steels fatigued in air [25]. Kunio et al. [25] have related this to precipitation at these sites (prior austenitic grain boundaries) of a relatively narrow band of proeutectoid ferrite that affords little resistance to plastic deformation. Intergranular fatigue crack initiation was not observed for a low-alloy steel (2.08Ni, 0.28Cr) due apparently to the role of alloying elements in delaying proeutectoid ferrite formation [26–27]. However, the carbon equivalent for this alloy was only slightly greater than for the QT108. This is consistent with absence of intergranular cracking for HY130 specimens in the present program (HY80 has not been analyzed). Also, the 930°C quenching temperature for QT108 [28] was in the range of intergranular fatigue crack initiation susceptibility determined by Kunio et al. On the basis of this rationale, fatigue properties of microalloyed quenched and tempered steels may encounter a tensile strength limit above which crack initiation shifts to an intergranular mode, whereas no such transition occurs for steels of higher alloy content.

Conclusions

1. Freely corroding fatigue strength of the nine steels investigated was approximately the same irrespective of composition, microstructure, or strength.

2. Cathodic polarization to -1.10 V (SCE) improved fatigue strength at higher cycles to initiation relative to the freely corroding value, in most cases, and reestablished an endurance limit.

3. Endurance limit at -1.10 V was proportional to tensile strength up to approximately 680 MPa and was approximately tensile strength independent beyond this. In the former regime, endurance limit was approximately 18% less than for comparable air data of others. However, limited air experiments in the present program suggested a smaller difference, compared to -1.10 V, than this.

4. A relatively low endurance limit was determined for QT108 at -1.10 V compared to its tensile strength. This was apparently due to intergranular fracture as opposed to quasicleavage for the other steels. Either inclusion debonding (alternately, a related microstructural feature) or proeutectoid ferrite precipitation at prior austenitic grain boundaries, or both, may have been responsible. This may indicate a strength limit for microalloyed quenched and tempered steels above which hydrogen can effect a fracture transition to a more brittle mode.









FIG. 21—Inclusion debonding in a QT108 specimen tested in seawater under cathodic protection ($\Delta K/\sqrt{\rho} = 475$ MPa).

a/W	ASTM E 647-83 and ASTM E 399-83	Current	% Difference
0.05	2.41	3.78	56.94
0.10	3.03	4.08	34.84
0.15	3.65	4.43	21.51
0.20	4.27	4.83	13.03
0.25	4.92	5.30	7.56
0.30	5.62	5.85	4.05
0.35	6.39	6.51	1.89
0.40	7.28	7.33	0.65
0.45	8.34	8.34	0.03
0.50	9.66	9.64	-0.21
0.55	11.36	11.34	-0.24
0.60	13.65	13.63	-0.20
0.65	16.86	16.83	-0.17
0.70	21.55	21.52	-0.16
0.75	28.86	28.82	-0.12
0.80	41.20	41.22	0.04
0.85	64.90	65.22	0.49
0.90	121.93	123.70	1.46
0.95	351.46	362.84	3.24

TABLE 5—(KB \sqrt{W})/P.

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Editors' Note

While the authors cite ASTM E 647-83 for their specimen configuration and preparation, they have used a solution for stress intensity calculation other than that which is cited in ASTM E 647-83 and ASTM Test Method for Plane-Strain Fracture Toughness of Metallic Materials (E 399-83). The stress intensity solution that is included in the current standards is based on the boundary collocation results of Newman and is the generally accepted standard solution developed by ASTM Committee E24 in the 1973 to 1974 time frame. The equation used by the authors provides stress intensity values that agree with the ASTM standards equations within 1% for a/W values between 0.4 and 0.85 as Table 5 shows.

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Cyclic Tension Corrosion Fatigue of High-Strength Steels in Seawater

REFERENCE: Jones, W. J. D. and Blackie, A. P., "Cyclic Tension Corrosion Fatigue of High-Strength Steels in Seawater," *Environmentally Assisted Cracking: Science and Engineering, ASTM STP 1049*, W. B. Lisagor, T. W. Crooker, and B. N. Leis, Eds., American Society for Testing and Materials, Philadelphia, 1990, pp. 447–462.

ABSTRACT: Four low-alloy steels with nickel contents varying from 0.2 to 4.0% (BS 970: 722M24, 817M40, 976M33, and 835M30) quench hardened and tempered to give yield or 0.2% proof strengths of approximately 800 MPa were tested in cyclic tensile loading (R = 0.05) at a frequency of 0.167 Hz in plain and notched (SCF = 2) forms in air, freely corroding in ASTM synthetic seawater (temperature 8°C and pH 8.2) and with cathodic protection of -850 mV and -1050 mV to establish S-N data for offshore platform design.

The steels suffered considerable reductions in fatigue performance in the freely corroding condition. Cathodic protection at -850 mV improved the performance of all four steels and in one case (817M40) restored it to that in air. Notched specimens were not improved to the same degree as plain specimens.

Cathodic protection at -1050 mV fully restored the fatigue performance of plain and notched steel 817M40 but the others showed a reduction in performance due to intergranular cracking in initiation and early crack propagation life in place of the otherwise ductile transgranular fracture; this was attributed to hydrogen absorption.

KEY WORDS: low-alloy steels, quenched and tempered high-strength steels, cyclic tension, corrosion fatigue, seawater corrosion, marine corrosion, cathodic protection, fatigue (materials), cracking, environmental effects

In recent years, a new type of oil production platform has been designed for use in the North Sea in which the legs are used in tension to tether the floating top structure to anchoring points on the sea floor; this is known as tension leg platform (TLP). The legs are normally pretensioned to some desired stress and in addition they experience a fluctuating stress due to the interaction of the platform with the sea. The strength level of the steel used on the one TLP in service (and considered for other designs) was so high, namely, up to 800 MPa, that quenched and tempered low-alloy steel was used for the construction. Such steels are not readily weldable because of their high carbon equivalent values and may be joined by threaded connections. As the steel is operating immersed in the sea, it must be cathodically protected, and it is therefore necessary to know the effect of cathodic protection on the corrosion fatigue behavior and to check that the higher protection potential of -1050 mV that may be used in service does not adversely affect the fatigue resistance.

When a high yield strength is required in heat-treated thick sections, it is necessary to select a steel with a high hardenability. The addition of nickel is widely favored for increasing the hardenability of steels, however, it has been reported that the presence of nickel in steel increases its susceptibility to stress-corrosion cracking and for this reason the National

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Association of Corrosion Engineers (NACE) standard MR-01-75 (1980 revision) restricts the use of nickel in steels for service in sour wells. It was therefore relevant to question whether the nickel content of steel to be used for cathodically protected tethers was an important consideration in selecting a steel.

The introduction of TLPs created the need for information on the cyclic tension fatigue strength of high yield strength steels in seawater with cathodic protection. At the outset of this project, a literature survey was carried out that revealed no information of this type. A program of testing was therefore set in motion. To simulate all of the practical features just mentioned, it was decided to carry out fatigue life (S-N) tests under the following conditions: cyclic zero to tension loading of plain and notched specimens at a frequency of 0.167 Hz in synthetic seawater at 8°C, freely corroding and with cathodic protection of -850 mV and -1050 mV on the following steels, all having a nominal yield strength of 800 MPa:

- 1. BS970 grade 722M24 containing 0.2% nickel,
- 2. BS970 grade 817M40 containing 1.6% nickel,
- 3. BS970 grade 976M33 containing 3.5% nickel, and
- 4. BS970 grade 835M30 containing 4.0% nickel

This work was partially reported earlier [1] when all four steels had not been tested. A detailed explanation of the testing procedure and S-N curves of three steels only were given at that stage. In this paper, the S-N data for the fourth steel is presented together with a comparison of the corrosion fatigue characteristics of all four steels and a fractographic survey.

This work is part of a continuing program in which the effect of variation of the stress ratio, R (= minimum stress/maximum stress), on S-N data has been determined and in which fatigue crack propagation rates have also been determined for some of the steels under varying conditions of cathodic protection and with various R values; these results will be published later.

Testing Procedure

Machines were constructed as shown in Fig. 1*a* to carry out low frequency zero to tension fatigue tests with a maximum load capacity of 30 kN. The mechanism of operation may be seen by referring to Fig. 1*a*; a mass of known weight is placed on the loading pan A and at D if desired, and is transmitted to the specimen via a series of linkages and a horizontal loading beam B pivoted about the position S, so that the load experienced by the specimen is approximately 15 times greater than that suspended at A and D.

Cyclic loading is achieved by periodically removing and replacing the load at A using an electro-hydraulic thruster situated below A. The power supplied to the thruster is controlled by an electric switching relay and is actuated by a set of adjustable timers that determine the duration of each forward and return stroke of the thruster, and thus the frequency of the test. When the position of the forward stroke is at its highest, the linkage at C is relaxed and the specimen experiences only static load suspended at D, if any. When the return stroke is at its lowest position, the load is freely suspended and the specimen experiences the full load. The forward and return strokes are further governed by an internal variable time lag control on each thruster and the required waveform may be obtained by adjusting these devices. The most desirable waveform was presumed to be sinusoidal and adjustments were made with a view to attaining this form, however, it was not possible to do so precisely. A typical loading waveform is shown in Fig. 1b.

A small constant load, 5% of the maximum load, was placed at D to ensure that the





FIG. 1-(a) Diagram of the fatigue testing machine and (b) load waveform.

specimen and linkages remained taut and to avoid "snatching" during take-up of the full load.

The fatigue test specimens were of two types: (1) plain specimens having a gage diameter of 6 mm and a gage length of 40 mm, or (2) notched specimens having a reduced parallel section of 8 mm diameter and a centrally located 2 mm diameter semicircular notch providing a stress concentration factor of 2.15 [2] on a 6 mm diameter minimum section. The gage surfaces of the plain fatigue specimens were longitudinally ground to produce a surface finish better than 0.5 μ m prior to testing.

The corrosion cell, made from PMMA (perspex), completely enclosed the test section with provision for the necessary measuring probes, and was attached as shown in Fig. 2. This design facilitated the continuous measurement of the corrosion potential or the application of cathodic protection to the specimen. All electrochemical potential measurements were made with respect to the saturated silver/silver chloride (Ag/AgCl) reference electrode.

Testing was carried out in a saline solution produced in accordance with ASTM Specification for Substitute Ocean Water (D 1141-86). The solution was continuously circulated through the corrosion cell at a flow rate of 100 mL/min and maintained at a temperature of 8°C.

Materials Tested

The chemical compositions of the four steels used are given in Table 1. Test pieces were machined from 722M24, 817M40, and 835M30 steel bars of nominally 25 mm diameter, commercially bought in a condition having measured yield strengths of approximately 880



FIG. 2—A section of the corrosion cell and fatigue specimen.

	722M24	817M40	976M33	835M30
Carbon	0.25	0.40	0.34	0.29
Silicon	0.20	0.29	0.27	0.23
Manganese	0.50	0.56	0.32	0.47
Sulfur	0.012	0.029	0.002	0.027
Phosphorus	0.012	0.010	0.008	0.014
Nickel	0.19	1.56	3.51	3.99
Chromium	3.21	1.09	1.43	1.15
Molybdenum	0.58	0.26	0.48	0.26
Vanadium			0.15	

TABLE 1—Chemical composition of steels (all the quantities shown are in percent by weight)

MPa and ultimate tensile strengths of 1000 MPa. The specimens were subsequently retempered by heating to 600°C for 2 h and air cooled to obtain the desired yield strength for this investigation, namely, 800 MPa. Steel BS 976M33, having a nominal yield strength of 800 MPa, was supplied in the form of rectangular sections, 75 by 75 by 630 mm, cut from a forged billet. Transverse and longitudinal hardness surveys were conducted on each section that confirmed the homogeneity of the steel.

The mechanical properties of these steels are given in Table 2. The data shown were obtained from tension test pieces machined as the plain fatigue specimens. Charpy V-notch specimens were machined in accordance with ASTM Methods for Notched Bar Impact Testing of Metallic Materials (E 23-86) and the average impact strength of each steel was determined at 0°C.

Metallographic examination and hardness testing were conducted on samples removed from the shoulder of the tension test specimens.

The microstructure of each steel exhibited a tempered martensite apearance. With the exception of Steel 976M33, the average prior austenite grain size of these steels was 30 to 40 μ m. Steel 976M33 exhibited a coarser prior austenite grain size of 140 μ m.

Results and Discussion

Fatigue Tests

Fatigue tests were carried out on all four steels under the following conditions:

1. in air,

2. freely corroding,

	722M24	817M40	976M33	835M30
Yield stress, MPa		802		
0.2% proof stress, MPa	785		798	791
Ultimate tensile strength, MPa	898	910	905	918
Fracture strain	0.104	0.142	0.094	0.102
Modulus of elasticity, GPa	216	207	206	210
Reduction in area, %	73.4	66	70	63
Vickers hardness VHN20				
(average of three values)	277	284	287	265
Impact strength—Charpy V notch, 0°C (J)				
minimum value	148	133	130	76
average of three specimens	151	135	131	79

TABLE 2-Mechanical test data for steels (average of two specimens except where stated otherwise).



FIG. 3-S-N data for Steel 835M30. Plain specimens tested in air and synthetic seawater.

- 3. cathodically protected at a constant potential of -850 mV, and
- 4. cathodically protected at a constant potential of -1050 mV.

The S-N data obtained using plain and notched specimens of Steel 835M30 only are given in Figs. 3 and 4, respectively. The results obtained from testing plain specimens in air show that a reduction in the cyclic stress level from 830 MPa to fatigue limit of 730 MPa corresponded to an increase in the fatigue life from 4×10^4 to 4.6×10^5 cycles to failure. The fatigue life curve for this finite life region, as shown in Fig. 3, has a gradient of 4.72×10^{-2} . The fatigue resistance of unprotected specimens, freely corroding in seawater, was signifi-



FIG. 4-S-N data for Steel 835M30. Notched specimens tested in air and synthetic seawater.

cantly lower, exhibiting a reduction in the failure stress from 815 MPa at 5×10^4 cycles, to 300 MPa at 10^6 cycles to failure. The linear regression curve containing this data has a gradient of 0.273 and a correlation coefficient of 0.80. The application of cathodic protection using an applied potential of -850 mV restored the fatigue resistance of the material to a level comparable with the air test data, and in the high cycle regime the fatigue strength exceeded the air test value. The fatigue stress-life curve for this data has a gradient of 2.95×10^{-2} . Increasing the applied potential from -850 to -1050 mV was less effective in restoring the fatigue strength, and resulted in a reduction in the fatigue resistance at cyclic stress levels above the fatigue limit. The fatigue-life curve representing this data has a gradient of 0.157 and a regression coefficient of 0.97.

The cyclic tension fatigue life curve obtained for notched specimens tested in air is shown in Fig. 4. Over the stress range investigated, from 750 MPa to a fatigue limit of 400 MPa, the fatigue life increased from 6×10^3 to 2×10^5 cycles to failure, the linear regression curve having a gradient of 0.175 and a regression coefficient of 0.99. The results obtained from corrosion fatigue tests of unprotected specimens in seawater show a continuous reduction in the fatigue strength from 700 to 65 MPa over the fatigue life range of 10^4 to 10^6 cycles. The effect of cathodic protection at both -850 and -1050 mV was similar, improving the fatigue resistance and restoring the fatigue limit, although the fatigue strength was lower than the level observed in the air test results. At high cyclic stresses, cathodic protection produced an adverse effect, lowering the fatigue strength below the level obtained from unprotected specimens freely corroding in seawater. The fatigue life curve between the cyclic stress range of 650 MPa and the fatigue limit of 320 MPa has a gradient of 0.157 and a regression coefficient of 0.97.

The S-N data of the type shown in Figs. 3 and 4 can be presented in an alternative form that shows more clearly the effect of cathodic protection on the fatigue resistance. This can be seen in Fig. 5 that shows the fatigue stress range to cause fracture of the steel for various lives plotted against the specimen electrochemical potential. The data points plotted in Fig. 5 are taken from the averaging curves drawn in Figs. 3 and 4. The air fatigue data have been given an arbitrary position on the abscissa to facilitate the comparison. With these curves, it is possible to see at a glance if the use of cathodic protection has been successful in returning the corrosion fatigue performance from that for the freely corroding condition on the right to that obtained in air on the left. In addition, it can be seen if cathodic protection has then been reduced by the application of more negative values of potential.

The effects of free corrosion and cathodic protection on fatigue behavior of the three steels (722M24, 817M40, and 976M33) are shown in Figs. 6, 7, and 8 using the same form of representation as for Steel 835M30 in Fig. 5.

Comparison of the results obtained for the four steels shows that in every case testing in seawater without protection lowered the fatigue resistance considerably. The decrease in fatigue strength was approximately equal in three of the steels, with 976M33 showing a less severely reduced strength at long lives.

Cathodic protection restored the fatigue strength towards that of air but not completely in all cases. A cathodic potential of -850 mV improved the fatigue strength of all steels in every condition and at all lives, but only plain specimens of 817M40 achieved full restoration to air values. Further change of the potential to -1050 mV caused no deterioration in the performance of plain specimens of 817M40 and improved the performance of notched specimens to that of air notched values. In the case of this steel only, the use of this value of cathodic potential was totally successful in restoring the fatigue behavior to that of air in all conditions. When the potential was changed to -1050 mV for the other three steels, they all showed varying degrees of deterioration in fatigue performance as can be seen in



FIG. 5—The fatigue strength of Steel 835M30 in air, freely corroding at -580 mV in synthetic seawater and cathodically protected at -850 and -1050 mV.

Figs. 5, 6, and 8. As a result, none of them fully achieved the restoration of fatigue properties to those in air; this deterioration was most pronounced for Steel 976M33.

It may be clearly seen in the fatigue results that the improvement in fatigue performance produced by cathodic protection is not as great on notched specimens as it is on plain. At this stage of completion of the project, it is not possible to explain this feature, however, work is continuing on the measurement of fatigue crack initiation lives and crack propagation rates that may throw some light on this problem.

The four steels tested form a group having the same strength and metallurgical treatment (quench hardening and tempering) but having different chemical compositions. This allows a comparison to be made of the influence of composition on the deterioration in fatigue properties in seawater (compared with air) and the degree to which the properties can be restored by the application of cathodic protection. These steels were chosen to have a variation in nickel from approximately 0 to 4%, but it was not possible to have all the other elements present maintained at constant compositions. Nevertheless, if the data are considered for any significant effect that can be related to composition, it is possible to find the correlation illustrated in Fig. 9. This shows the relationship of nickel content to the fatigue strength of the four steels cathodically protected in seawater expressed as the percentage reduction in the air fatigue strength at a life of 10^6 cycles. On the basis of this small number of cases, it appears that there is an optimum performance that occurs at a critical nickel content that decreases with increase in negativity of the cathodic potential.



FIG. 6—The fatigue strength of Steel 722M24 in air, freely corroding at -590 mV in synthetic seawater and cathodically protected at -850 and -1050 mV.

The deterioration of fatigue strength with increasingly negative values of cathodic potential is commonly assumed to be due to the reduction in fracture ductility of steels by absorbed hydrogen. If this is so, then it is difficult to see why the best performance occurs at a certain value of nickel content and that both more or less nickel weakens the steels. It may be that other elements present have interactive effects that confuse an interpretation based on nickel alone.

Fractography

Fracture surfaces of all four steels were studied in the scanning electron microscope (SEM) after testing in all environmental conditions and over a range of stresses. From the very large number of observations made and photographs taken [3], certain general features emerged. In order to minimize the number of photographs reproduced here, the findings will be presented in a summarized form.

In all four steels, the air fatigue fractures were remarkably similar in appearance, they did not change significantly with variations in stress, and they did not vary during the progress of the crack across the fracture surface at any one cyclic stress range. Fatigue crack initiation in air tests was found in all cases to have occurred at the intersection of, or in very close proximity to, a nonmetallic inclusion and the surface, as shown in Fig. 10 (Steel 976M33); this confirms previous observations on high-strength low-alloy steels [4]. The fatigue crack



FIG. 7—The fatigue strength of Steel 817M40 in air, freely corroding at -620 mV in synthetic seawater and cathodically protected at -850 and -1050 mV.

then propagated by transgranular ductile tearing uninfluenced by microstructural features. A typical fracture surface is shown in Fig. 11 that is Steel 817M40 tested in air at a stress of 780 MPa; the crack has moved from right to left at 30° to the bottom of the figure as indicated by the arrow. The fracture shows irregular ridges running parallel to the direction of movement of the crack and very fine fatigue striations approximately at right angles to that direction.

In Steels 722M24, 976M33, and 835M30 tested in seawater without cathodic protection, crack initiation was mainly due to interfacial separation along grain boundaries rather than at corrosion pits on the specimen surface, and extended approximately one grain diameter normal to the external surface, as shown in Fig. 12. As the fatigue crack depth increased, the proportion of intergranular fracture diminished; this may be attributed to either a reduction in the environmental influence at higher growth rates or with an increase in the local plastic deformation ahead of the advancing crack interface or both. The change in the fracture mode from intergranular to mixed intergranular-transgranular type was accompanied by an apparent increase in the incidence of secondary cracking, which was probably associated with limited fracture along the interface of prior austenite grains.

Although the failure mechanism of Steel 817M40 in air was similar to the other steels, it differed from them in seawater; brittle fracture along grain boundaries was not observed on the fracture surfaces of specimens tested under freely corroding conditions. The absence of microstructural sensitive cracking may be related to the higher ductility or possibly the



FIG. 8—The fatigue strength of Steel 976M33 in air, freely corroding at -530 mV in synthetic seawater and cathodically protected at -850 and -1050 mV.



FIG. 9—The effect of variation in nickel content on the fatigue strength of the four steels cathodically protected in seawater, expressed as the percentage reduction in the air fatigue strength for a life of 10⁶ cycles.



FIG. 10-Steel 976M33 tested in air at a cyclic stress range of 780 MPa.

lower interfacial microsegregation of this steel or both. The mode of failure at higher stress levels was similar to the quasi-static type fracture along martensite lath boundaries observed by Kameda and McMahon [5], although at lower stresses this was replaced by ductile striation-transgranular fracture of the matrix.

Intergranular separation as shown in Figs. 13 and 14 for Steels 722M24 and 835M30, respectively, was evident on the fracture surfaces of all the steels tested in seawater with cathodic protection with the exception noted in the next paragraph. These micrographs were recorded at locations close to the initiation site of each specimen and show that for Steel



FIG. 11-Steel 817M40 fatigue tested in air at a cyclic stress range of 780 MPa.



FIG. 12—Steel 722M24 tested in seawater with cathodic protection of -1050 mV, at a cyclic stress range of 775 MPa.

722M24 fatigue crack propagation occurred primarily along the interface of the prior austenite grain boundaries. Steel 835M30, however, exhibits a mixed-mode failure, with intergranular facets interspersed by regions of ductile transgranular fracture. In Steel 976M33, intergranular fracture was accompanied by brittle cleavage of the matrix along inter-lath and lath packet boundaries, as shown in Fig. 15. The occurrence of intergranular and, in some cases, cleavage fracture in these steels diminished as the crack depth increased. This



FIG. 13—Steel 722M24 tested in seawater with cathodic protection of -1050 mV, at a cyclic stress range of 770 MPa.



FIG. 14—Steel 835M30 tested in seawater with cathodic protection of -1050 mV, at a cyclic stress range of 770 MPa.

suggests that the environmental influence on the fracture process was confined to the near surface region.

Environmentally assisted fracture of the type just identified was only observed in Steel 817M40 at the higher potential of -1050 mV and at lower stress levels. However, in those instances where the fatigue strength was restored to the same level as that obtained in the air test, then the occurrence of intergranular failure on the fracture surface of cathodically



FIG. 15—Steel 976M33 tested in seawater with cathodic protection of -1050 mV, at a cyclic stress range of 765 MPa.

protected specimens diminished and was replaced by a ductile transgranular cracking mode, similar in appearance to the fracture observed in the air test.

Fractographic observations have revealed that significant differences in the fracture surfaces of these steels were identified in the vicinity of the crack initiation site. The available evidence suggests that when cathodic protection restores the corrosion fatigue strength to the level obtained in air tests there is no discernible change in the mechanism of fatigue fracture. Thus, it follows that the reduction in fatigue strength caused by cathodic protection may be related to either a reduction in crack initiation resistance or an increase in the rate of early-stage fatigue crack propagation, associated with microstructural-sensitive intergranular cracking or both. The sensitivity of similar medium and high-strength steels to intergranular brittle fracture along prior austenite grain boundaries has been widely reported [6,7] and has been associated with environmental interactions causing a lowering of the cohesive strength along an interface already weakened by segregated impurities. In saline solutions and natural seawater environments, these effects have been associated with a hydrogen embrittlement mechanism that may be promoted by either low pH, causing an increase in hydrogen ion concentration, or hydrogen evolution generation by applied cathodic potentials or hydrogen sulfide containing environments. The correlation between the incidence of intergranular separation and environmentally assisted cracking, particularly with lower applied stresses, is also consistent with previous observations on the fracture characteristics of structural steels [8].

Beneficial effects have been reported on crack growth in structural steels under cathodic protection that have been ascribed to the "wedging" action of calcareous deposits on the interior surfaces of the fatigue crack, thereby reducing the effective dynamic stress amplitude [8]. The fracture surfaces of the steels examined in this investigation showed no evidence of calcareous deposits, although significant deposition occurred on the gage surface of the specimens, particularly at the more electronegative potentials.

In unprotected corrosion fatigue tests, microstructural sensitive cracking was also observed, although less confinied, at regions contained within the initial stages of crack development. Clearly, the operative failure mechanism was less dominated by the crack initiation resistance; however, the evidence suggests that the growth of small fatigue cracks (particularly at lower stress levels) was the rate-controlling factor of the fatigue process.

The suggestion that the effect of the environment is more important in crack initiation and the early stages of crack extension, rather than in the subsequent propagation stage in the fatigue process, is supported by others in work on structural [8] and high-strength steels [9-11]. These results are of a similar type showing either a considerable reduction in the stress intensity of the fatigue crack growth threshold or an inflexion in the crack growth rate curve at near threshold levels. However, a substantial body of work exists that shows accelerated fatigue crack growth rates at all stress intensity levels, for high-strength steels tested in hydrogen-containing environments.

Summary

The study of Steels BS970:722M24, 817M40, 976M33, and 835M30 has shown that their cyclic tension fatigue properties when unprotected and freely corroding in seawater are considerably reduced compared with their fatigue response in air. The fatigue strength of plain specimens at 10⁶ cycles to failure was lowered by at least 50% compared with the air test data, and the notched fatigue strength under the same test conditions was even more adversely affected; for Steels 817M40, 722M24, and 835M30, the failure stress was lowered by a factor of ten. It was also noticeable that under corrosion fatigue conditions with the exception of 976M33, these steels do not exhibit an endurance limit as commonly found in

air tests; consequently, the failure stress for high cycle fatigue, that is, typically in-service periods greater than 10^6 cycles, is extremely low. The notched fatigue response of Steel 976M33 was different in this respect exhibiting a higher cyclic strength at 10⁶ cycles than the other steels, due to retaining its fatigue limit.

The effect of cathodic protection at -850 mV on plain specimens was to restore the fatigue properties of 835M30 and 817M40 to the air fatigue level and the other two steels to near air performance. In all cases, the fatigue properties of notched specimens were not restored to the same degree as the plain specimens.

Cathodic protection at -1050 mV restored the fatigue properties of Steel 817M40 in plain and notched forms to their air performance. Plain 722M24 was further improved but the notched form was not. Steels 835M30 and 976M33 had their fatigue performances reduced by changing the cathodic potential to -1050 mV.

The reduction in fatigue properties due to cathodic protection appears to be related to the nickel content of the steels, but it is not possible to arrive at a definite conclusion because of the variation in the other elements present. Cathodic protection restored the fatigue performance to that in air for 3.5% nickel-containing steel at -850 mV and for 1.6% nickelcontaining steel at -1050 mV; all other compositions had their properties restored to a lesser degree or reduced.

An SEM fractographic study showed that initiation of fatigue cracks in air tests occurred preferentially at the intersection of nonmetallic inclusions and the surface of the specimen, and propagation was by transgranular ductile tearing. A reduction in fatigue strength by corrosion or corrosion protection was associated with the incidence of grain boundary cracking or brittle quasi-cleavage of the matrix or both. This change in fracture mechanism was probably due to the influence of absorbed hydrogen.

Acknowledgment

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Fatigue Crack Growth Behavior of Different Stainless Steels in Pressurized Water Reactor Environments

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ABSTRACT: An experimental program has been conducted in order to determine the fatigue crack growth rate (FCGR) curves of different stainless steels for nuclear pressure vessels and pipings in pressurized water reactor environments and to define reference fatigue crack growth rate curves for these materials. The parameters studied are: the steel structure, the load ratio (R), and the water chemistry. A slight, but clear effect of environment was observed for the five steels studied. The paper presents the FCGR curves and the fractographic examinations for the different testing conditions and stresses the differences between FCGR behavior of stainless steels and low-alloy steels.

KEY WORDS: corrosion fatigue, fatigue crack growth, stainless steels, water chemistry, fatigue (materials), cracking, environmental effects

Stainless steels are utilized widely in a number of components for the primary coolant of a pressurized water reactor. Such components may be subjected to cyclic loadings in service that could cause growth of flaws or cracks. Linear-elastic-fracture-mechanics (LEFM) concepts are used to evaluate the crack growth of these flaws, and LEFM methods are presently included in Section XI of the ASME Boiler and Pressure Vessel Code. The Section XI curves, however, are now only applicable to low-alloy ferritic pressure vessel steels [1]. Since stainless steels are also utilized in pressure vessel and piping applications, there is a need to define reference fatigue crack growth rate (FCGR) curves for these materials. In the 1970s, considerable work was done in characterizing the effect of various parameters (for example, waveform, temperature, steel composition, water chemistry, etc.) on the fatigue-crack propagation of low-alloy ferritic pressure vessel steels [2-11].

Several effects are now well established and research is continuing to explain certain phenomena peculiar to this metal-environment system. The fatigue crack growth of lowalloy steels includes two types of behavior illustrated by Fig. 1: (1) a single slope fatiguetype curve, for the non-sensitive materials; and (2) a two-slope corrosion-type curve with a rapid increase of the FCGR and a stabilization region (plateau) for the sensitive materials.

One of the most significant parameters appears to be the sulfur content of the materials. Sulfur contents below 0.010% lead to a fatigue-type behavior, whereas sulfur contents greater

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FIG. 1—Schematic FCGR behavior of low-alloy pressure vessel steels.

than 0.015% lead to a corrosion-type behavior [6]. Figure 2 illustrates such behavior where the A533B steel containing 0.018% sulfur gives a corrosion-type behavior.

Figure 3 shows the effect of the waveform: for intermediate sulfur content materials (0.010 < S < 0.015%), the sinusoidal waveform is the most detrimental one among the usual waveforms used [6].

The effects of the loading ratio, $R = P_{\min}/P_{\max}$ (up to 0.9), and frequency (down to 0.1 cpm) on low sulfur materials (Fig. 4) are limited [8].

As the upper bounds of the data sets on pressure vessel steels become better defined [1,11], some studies have shifted to the behavior of stainless steels [12-16]. In this context, an experimental program has been conducted in order to: (1) determine the fatigue crack growth rate curves of different stainless steels for nuclear pressure vessels and pipings in pressurized water reactor (PWR) environments, and (2) define reference fatigue crack growth rate curves for these materials.



FIG. 2-Effect of the sulfur content of the materials on the FCGR [6].

Experimental Procedure

Test Program

The parameters studied are:

- 1. the steel structure—different stainless steels, cast and forged, with austenitic, austenitic-ferritic, and martensitic structures;
- 2. the load ratio— $R = P_{\min}/P_{\max} = 0.1$ and 0.7; and
- 3. the water chemistry—two environments (P1 and P2), where the P1 environment corresponds to the nominal working conditions and the P2 environment corresponds to a pollution of P1 environment by oxygen and chlorides.

All tests were conducted with a sinusoidal waveform at a frequency of 1 cycle/min.



FIG. 3—Effect of the waveform on the FCGR of a material containing 0.013% sulfur (R = 0.2) [6].

Materials

The five stainless steels that were studied include the following.

- 1. An austenitic steel, containing 17Cr-12Ni, of Type 316 with niobium, used for internal bolting, in the form of a forged bar, quenched from 1100°C.
- 2. An austenitic steel, containing 23Cr-17Ni, used for internal bolting and tube support plate, in the form of a forged plate, quenched from 1100°C. It has higher mechanical properties than Type 316 steel and also a larger grain size.
- 3. A precipitation-hardenable austenitic steel, containing 25Ni-15Cr, used for internal bolting, in the form of a forged bar, quenched from 925/1025°C and tempered 16 h at 725°C.
- 4. An austenitic-ferritic steel, containing 21Cr-8Ni, used for primary piping, in the form of a cast pipe, quenched from 1100°C.
- 5. A martensitic steel, containing 17Cr-4Ni-1Mo, used for internal bolting, in the form of a forged bar, quenched from 1100°C and tempered at 550/625°C.



FIG. 4—Effect of the load ratio on the FCGR of a low sulfur content material (sulfur = 0.009%) [8].

The chemical compositions are presented in Table 1. The martensitic steel contains 0.019% S, which would be considered high for a low-alloy steel [6,11].

The tensile properties have been determined with specimens oriented in the T-L orientation for plates and bars, and in the axial direction for the cast pipe; and they are presented in Table 2. These properties present a large variation. For instance, the yield stresses at 300°C vary from 200 to 700 MPa.

Specimens

Standard compact-type (CT) specimens for fatigue crack growth rate testing were used (25 mm thick for tests at R = 0.1 and 50 mm thick for tests at R = 0.7). The fatigue crack plane was oriented as follows:

- 1. parallel to the longitudinal rolling direction (plates) or axis of forging (bars) and perpendicular to the direction of loading (T-L orientation), and
- 2. perpendicular to the axial direction (cast pipe).

C Mn Si S P Ni Cr Mo Cu Nb N vi 0.086 1.63 0.41 0.002 0.023 13.3 17.57 2.3 0.052 0.78 vi 0.027 5.56 0.041 0.001 0.021 15.3 22.48 2.9 0.054 0.26 0.4 T 0.031 1.516 0.069 0.002 0.015 26.06 15.08 1.18 0.036 <0.01 0.07 Mo 0.049 0.875 0.28 0.019 0.017 4.43 15.14 0.8 0.09 0.07				TABLE	1-Chemica	l compositio	n (percent b	y weight).				
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		C	Mn	Si	s	Ч	ïŽ	ŗ	Mo	Cu	qN	z
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.086	1.63	0.41	0.002	0.023	13.3	17.57	2.3	0.052	0.78	:
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.027	5.56	0.04	0.001	0.021	15.3	22.48	2.9	0.054	0.26	0.4
i 0.031 0.66 0.8 0.001 0.018 7.83 21.24 2.5 0.084 0.07 Mo 0.049 0.875 0.28 0.019 0.017 4.43 15.14 0.8 0.09	5	0.031	1.516	0.669	0.002	0.015	26.06	15.08	1.18	0.036	< 0.01	:
Mo 0.049 0.875 0.28 0.019 0.017 4.43 15.14 0.8 0.09	i	0.031	0.66	0.8	0.001	0.018	7.83	21.24	2.5	0.084	:	0.07
	Mo	0.049	0.875	0.28	0.019	0.017	4.43	15.14	0.8	0.09	:	:

_					
Steel	Temperature	0.2% Yield Strength, MPa	Ultimate Tensile Strength, MPa	Elongation in 50 mm Gage, %	Reduction of Area, %
17Cr-12Ni	RT ^a	278	596	52	70
	300°C	196	478	>39	64
23Cr-17Ni	RT	439	792	50	61
	300°C	256	623	49	60
25Ni-15Cr	RT	774	1060	≥ 24	41
	300°C	701	962	≥ 20	40
21Cr-8Ni	RT	364	600	32	65
	300°C	264	526	32	66
17Cr-4Ni-1Mo	RT	655	938	67	67
	300°C	692	854	54	54

TABLE 2—Tensile properties.

 a RT = room temperature.

Test Environments

The specifications of Environments P1 and P2 are listed in Table 3. The P1 environment is the nominal environment, containing chloride and oxygen below 0.1 ppm. The P2 environment corresponds to a pollution of the P1 environment by 1 ppm of oxygen and 0.5 ppm of chloride. The specified pH at room temperature, obtained by the addition of LiOH, is higher than the pH normally specified for PWR tests [8].

Experimental Technique

The FCGR tests have been carried out on servo-electrohydraulic machines, in autoclaves designed to operate at a temperature of 300°C and a pressure of 140 bars. The tests in Environment P1 ($O_2 < 0.1$ ppm) are performed in static autoclaves, that is, without water circulation. In these autoclaves, the oxygen is consumed on the walls and rapidly reaches levels of about 10 ppb. The tests in Environment P2 ($O_2 = 1$ ppm) are performed in low flow rate circulating autoclaves.

The specimen crack length was measured by a compliance technique. The face opening displacement of the specimen was monitored continuously using a linear variable differential transformer (LVDT), made of stainless steel, attached to the lips of the specimen, and located inside the autoclave. The face opening, δ , was converted during the test to crack length, *a*, through the relationships given by Hudak and Saxena [17].

Specifications	Environment P1	Environment P2
Temperature	300°C	300°C
Pressure	140 bars	140 bars
$pH(RT^a),$		
obtained by addition of LiOH	9.5 < pH < 10.2	9.5 < pH < 10.2
Cl	<0.1 ppm	0.5 ppm
O ₂	<0.1 ppm	1 ppm

TABLE 3-Test environments.

^a RT = room temperature.

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After the test, the calibration curve is checked with the initial and final crack fronts. This provides a calibration curve for each test. The crack length versus cycles data is then converted to crack growth rate versus range of applied stress intensity factor. Both the testing methods and the data processing procedures followed ASTM Test Method for Measurements of Fatigue Crack Growth Rates (E 647-88).

Metallurgical Examinations

Metallurgical examinations were performed by scanning electron microscopy and electron microprobe analysis. In fractography, the rupture surfaces of the specimens exhibit, in general, striationless features and cleavage-like fracture or striations that have different configurations. A consensus on the terminology and the definition of "ductile" and "brittle" striations has been established within the International Cooperative Group on Cyclic Crack Growth Rate [18]. Brittle striations have been defined as opposed to ductile striations, although in all cases a ductile mechanism of striation formation operates. This terminology was adopted to characterize the fractographic examinations presented here.

Results

21Cr-8Ni Austenitic-Ferritic Steel

Figure 5 shows the results obtained on the austenitic-ferritic cast steel in air at room temperature and at 300°C, and in Environments P1 and P2 at R = 0.1, where

- 1. in air, the temperature has no influence on the FCGR;
- 2. the curves obtained in the environment are parallel to the curves obtained in air, and shifted by a factor of about 3, which indicates a slight but clear effect of environment; and
- 3. the results obtained in Environments P1 and P2 are very close: a pollution of the P1 environment by 1 ppm oxygen and 0.5 ppm chlorides does not seem to affect the FCGR.

Fractographic examinations (Fig. 6) have shown that the fracture surfaces in air and in Environments P1 and P2 are essentially ductile. Fatigue striations appear for FCGR $da/dN > 10^{-4}$ mm/cycle (Figs. 6b and d). We have noted the presence of numerous inclusions (oxides). These inclusions do not seem to locally modify the fracture surface (Figs. 6b and d). In Environments P1 and P2, we have not noted a preferential attack of either phases (austenite or ferrite).

17Cr-12Ni Austenitic Steel

Figure 7 shows results obtained on the 17Cr-12Ni austenitic steel in Environments P1 and P2 at R = 0.1 and in Environment P1 at R = 0.7, where

- 1. at R = 0.1, the results obtained in Environments P1 and P2 are practically equivalent; and
- 2. in Environment P1, the FCGR increases when the R ratio increases from R = 0.1 to R = 0.7.



Fractographic examinations (Fig. 8) have shown:

- 1. fracture surfaces of the same type on the specimens tested in Environments P1 and P2, at R = 0.1, where the general ductile aspect is shown in Fig. 8*a*, and the ductile striations for FCGR $da/dN > 5 \times 10^{-4}$ mm/cycle are shown in Fig. 8*b*; and
- 2. in Environment P1, at R = 0.7, the surface appears more brittle than that observed at R = 0.1, where the aspect evoking that of planar facets and rivers is shown in Fig. 8c.

23Cr-17Ni Austenitic Steel

Figure 9 shows the results on the 23Cr-17Ni austenitic steel, in Environment P1 at R = 0.1 and 0.7, and in Environment P2 at R = 0.7, where




FIG. 6-Continued.



FIG. 7—FCGR curves of 17Cr-12Ni steel.

- 1. the results obtained in Environment P2 are very close to the results obtained in Environment P1 where pollution of the P1 environment by 1 ppm oxygen and 0.5 ppm chlorides does not seem to affect the FCGR, and
- 2. the FCGR increases when R ratio increases from R = 0.1 to R = 0.7.

Fractographic examinations (Fig. 10) have shown:

- 1. in Environment P1, at R = 0.1, the fracture surface presents a brittle general aspect, with features evoking cleavage and rivers (Fig. 10*a*), and ductile and brittle striations (Fig. 10*b*); and
- 2. in Environment P2, at R = 0.7, the general aspect appears more brittle than that observed at R = 0.1, in particular, where the striations are essentially of the brittle type (Fig. 10d).

∆K ~ 50,6 MPa√m Env. P1 - R = 0.10000 (P) 17Cr-12Ni steel FIG. 8-Microfractographs of 17Cr-12Ni austenitic steel. x 1010 REP268 ∆K ~ 22.9 MPa√m Env. PI - R = 0.199999 03E2 -17Cr-12Ni steel x 203





FIG. 9-FCGR curves of 23Cr-17Ni martensitic steel.

17Cr-4Ni-1Mo Martensitic Steel

Figure 11 presents the results on the 17Cr-4Ni-1Mo martensitic steel in Environment P1 at R = 0.1 and 0.7, and in Environment P2 at R = 0.1. The figure shows:

- 1. an influence of the Environment P2 greater than that observed on the other steels where the da/dN- ΔK curve, obtained Environment P2, shows a corrosion-type behavior with a double slope; and
- 2. in Environment P1, we notice the same trend concerning the R ratio.

Fractographic examinations (Fig. 12) have shown essentially ductile features with ductile striations in Environments P1 and P2. The ferrite zones (Fig. 12b) and the MnS inclusions that elongated normal to the fracture surface (Figs. 12a and c) do not locally modify the fracture. Furthermore, at R = 0.7, we have noted secondary cracks, where the density increases with ΔK .







FIG. 11-FCGR curves of 17Cr-4Ni-1Mo steel.

25Ni-15Cr Precipitation-Hardenable Austenitic Steel

Figure 13 shows the results on the 25Ni-15Cr austenitic steel, at R = 0.1 in Environments P1 and P2, and at R = 0.7 in Environment P1:

- 1. at R = 0.1, the results obtained in Environments P1 and P2 are very close, where the $da/dN-\Delta K$ curves present a clear plateau for $20 < \Delta K < 40$ MPa \sqrt{m} ; and
- 2. in Environment P1, the FCGR obtained at R = 0.7 are higher than the FCGR obtained at R = 0.1, according to the general trend observed in this program.

Fractographic examinations of specimens tested in Environments P1 and P2 at R = 0.1 (Fig. 14) have shown that:

1. in the plateau region $(20 < \Delta K < 40 \text{ MPa}\sqrt{m})$, the fracture occurs essentially by cleavage (Fig. 14*a*); we also notice the presence of planar facets and rivers; and









2. for $\Delta K > 40$ MPa \sqrt{m} , the fracture occurs by cleavage (Fig. 14c) and also brittle striations (Fig. 14b).

Discussion of the Results

In order to identify parameters that have a significant effect and to define reference curves, the results have been plotted as a function of the Environments P1 and P2 and as a function of the R ratio, R = 0.1 and 0.7, where:

- 1. in Environment P1 (Fig. 15), only the precipitation-hardenable austenitic 25Ni-15Cr steel presents a plateau behavior;
- 2. in Environment P2 (Fig. 16), the precipitation-hardenable austenitic 25Ni-15Cr steel presents a clear plateau behavior, and the austenitic-ferritic 21Cr-8Ni and the martensitic 17Cr-4Ni-1Mo steels present only a tendency towards this type of behavior;







- 3. for the same R ratio, the classification of the steels is the same in Environments P1 and P2.

Figure 17 presents the results obtained on the five materials, by identifying only the environment and the R ratio. It clearly shows:

- 1. no significant effect of the environment, since for the same R ratio, the results obtained in Environment P1 (circle points) and Environment P2 (triangle points) are close; and
- 2. a clear effect of the R ratio (open points for R = 0.1 and closed points for R = 0.7).



FIG. 16—Results obtained in Environment P2 at R = 0.1.

In these conditions, in order to define references curves, the results have been plotted as a function of the R ratio only (Fig. 18).

In order to take into account this effect, the FCGR da/dN has been expressed as a function of $\Delta K_{\text{eff}} = \Delta K/(1 - R/2)$. This relationship has been used by Bernard [13] for austenitic stainless steels in air at 300°C for R ratios up to 0.9. Figure 19 shows that this expression leads to a reduced scatterband of the results. The upper bound of air results, proposed by Bernard [13], is plotted on this figure. This upper bound underestimates the results obtained in this study, at $\Delta K < 30$ MPa \sqrt{m} .

The overall results have been adjusted by a relationship in the form: $da/dN = Cx(\Delta K)n$. The relationships obtained are (Fig. 20):



FIG. 17—Results obtained in Environment P1 and P2 at R = 0.1 and 0.7.

Mean curve: $da/dN = 7.726 \times 10^{-7} \times (\Delta K)1.754$ Upper bound: $da/dN = 2.318 \times 10^{-6} \times (\Delta K)1.754$ Lower bound: $da/dN = 2.575 \times 10^{-7} \times (\Delta K)1.754$

The scatter of the results varies from 1 to 9, which is relatively limited for this type of test, given the wide variation of the metallurgical structures and the mechanical properties of the steels studied.

Figure 21 compares all results with the present ASME Code curves [1] relative to low-



FIG. 18—Results obtained at R = 0.1 and 0.7.

alloy steels. This figure shows that these curves constitute an upper limit of the results obtained to date. They may be not conservative for results obtained at high R ratios (R > 0.7) or low values of ΔK ($\Delta K < 9$ MPa \sqrt{m}), or both.

The FCGR behavior of stainless steels has shown a certain number of differences with that of low-alloy steels:

1. Chemical Composition—It has been shown that the sulfur content plays an essential role in the FCGR of low-alloy steels [6, 11]. The martensitic steel 17Cr-4Ni-1Mo, which has a sulfur content of 0.019% considered as high sulfur for a low-alloy steel, gave a low FCGR.



Thus, it seems that the sulfur contained in the steel does not play the same role in stainless steels and in low-alloy steels.

2. Water Chemistry—Figure 22 shows the pollution effect of the PWR environment obtained on low-alloy steels in a previous study [9,10] where

- 1. pollution of chlorides and caustic soda without oxygen has no effect,
- 2. the presence of 1 to 3 ppm oxygen increases the FCGR by a factor of about 10, and
- 3. the simultaneous addition of chlorides and oxygen give the same results as oxygen



alone. In the case of stainless steels, a pollution of Environment P1 by 1 ppm oxygen and 0.5 chlorides does not affect the FCGR in a significant manner.

3. Loading—The effect of the R ratio is more pronounced in the case of stainless steels than in low-alloy steels in the same range of FCGR.

Conclusions

A slight, but clear environmental effect was observed for the five steels studied. The effect of the different parameters can be summarized as follows.



FIG. 21-Comparison of all results with the present ASME Code curves [1] relative to low-alloy steels.

Structure of the Steel

In Environment P1, only $25N_{1}-15C_{7}$ steel presents a plateau behavior. In Environment P2, $25N_{1}-15C_{7}$ presents a clear plateau behavior, and $21C_{7}-8N_{1}$ and $17C_{7}-4N_{1}-1M_{0}$ steels present only a tendency towards this type of behavior. For the same *R* ratio, the classification of the steels is the same in Environments P1 and P2.

Load Ratio

The R ratio has a pronounced effect. The expression of da/dN as a function of $\Delta K_{\text{eff}} = \Delta K/(1 - R/2)$ correctly takes into account the effect of the R ratio, since it reduces the scatterband of the results.



FIG. 22—A508C13 steel—effect of the pollution of PWR water [9,10].

Water Chemistry

A pollution of Environment P1 ($O_2 < 0.1$ ppm; Cl < 0.1 ppm) by 1 ppm $O_2 + 0.5$ ppm Cl does not affect the FCGR, in a significant manner.

Reference curves have been derived from all results. The scatter of the results varies from 1 to 9, which is relatively limited for this type of test, given the wide variation of the metallurgical structures and the mechanical properties of the steels studied.

The present ASME Code curves for low-alloy steels constitute an upper limit for the results obtained on stainless steels. They may not be conservative for high R ratios (R > 0.7) or low values of ΔK ($\Delta K < 9$ MPa \sqrt{m}), or both.

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Environmentally Assisted Cracking Behavior of a High-Level Nuclear Waste Container Alloy

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ABSTRACT: The environmentally assisted cracking behavior of cast ASTM A27 steel in a simulated groundwater environment was studied using both statically loaded and cyclically loaded specimens. The results show that, compared to other aqueous environments, the groundwater environment is relatively nonaggressive. The nonaggressive nature of this environment is believed to be related to its high pH and low level of dissolved oxygen.

KEY WORDS: fatigue (materials), cracking, environmental effects, nuclear waste storage, fatigue crack propagation, environmentally assisted cracking, cast carbon steel

The regulatory requirements for high level nuclear waste containment [1] state that the waste packages must exhibit "substantially complete containment" of stored waste radionuclides for 300 to 1000 years. Substantially complete containment has not been sufficiently quantified to provide requirements for the lifetime of any single specific waste package or for the precise distribution of lifetimes of the whole container population. However, it is clear that a large fraction of the whole container population will be expected to survive for at least 300 to 1000 years. The work described in this paper was in support of the Basalt Waste Isolation Project (BWIP), whereby the waste would be buried approximately 1 km deep in a formation of solid basalt rock.

The waste package design [2] will include three major components: (1) the waste form, (2) a metallic container, and (3) basalt/clay packing material enveloping the container to retard groundwater movement and radionuclide migration after eventual container breach. The present design includes a container of cast ASTM A27 Grade 60-30 carbon steel. It is felt that the large size of the containers would lead to casting as the most economical fabrication method. Earlier container design concepts employed wrought carbon steel plates formed into cylindrical shapes. Hence, this paper contains results for both A27 steel and ASTM A36 steel (the wrought equivalent of cast A27). Tests were also conducted on A36 steel weldments as well as the heat-affected zone (HAZ) of an A27 weldment. As shown in Fig. 1, the HAZ was configured in such a way as to maximize the probability of the crack propagating entirely within the HAZ.

The environment expected for the waste containers in a basalt repository will be relatively benign. However, the extremely long time frame for radionuclide containment required by

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FIG. 1-Macrophoto of a weld in cast A27 steel illustrating the "vertical" HAZ (on right side of weld).

the Nuclear Regulatory Commission (NRC) regulations of 300 to 1000 years makes behavior predictions for even a benign environment challenging. Initially, the waste packages will be exposed to temperatures as high as 250°C. The heat generation from the nuclear waste is the primary contributor; the ambient temperature at the approximately 1000 m depth planned for the repository is about 50°C. Over time, the decay heat generation will decline and the temperature of the waste containers for the bulk of the 300 to 1000 year containment period will be 100 to 150°C, dependent on the waste loading of the particular container. The external load on the container will be compressive in nature from the ambient hydrostatic pressure of 94 MPa. Some tensile stresses are possible on the external surface from discontinuity stresses near the container end and from residual stresses from closure welds. The magnitudes of the tensile stress have not been determined, but it is expected that the discontinuity stresses will be very low and that heat treatment will be employed to reduce residual stresses to a very low magnitude. Thus some tensile stresses will be probable at localized areas on the container external surface and could theoretically lead to environmentally assisted cracking (EAC) if they were of sufficient magnitude and the environment was sufficiently aggressive.

Characterization and prediction of EAC can be very difficult, especially in a weakly aggressive environment. This occurs because time for initiation and incubation of an EAC crack can be very long and yet the subsequent crack propagation rate can be sufficiently rapid to cause material failure. Thus, test and analysis methods for investigation of EAC must be very conservative and provide the most credible means of forecasting behavior for the container lifetime. In general, the approach is to use fracture mechanics testing to accelerate loading (compared to service environments) and fatigue-induced cracks to shorten incubation times. The objective of the testing will be to establish bounding material/environment conditions where EAC degradation will and will not occur. Then design and material choice can ensure that the waste container service conditions will be outside boundaries for EAC occurrence. Laboratory tests can only be conducted for a small fraction of the 300 to 1000 year containment period, however. Prediction of EAC behavior to the end of the

pH	9.7
\mathbf{F}^{-}	20
Cl-	398
SO4=	4
Total C	20
Ca	2
К	14
Na	349
Si	46

TABLE 1—Typical groundwater composition (units: mg/L except pH).

containment period must be enhanced by understanding of the mechanisms involved and incorporation of mechanisms in productive behavior models.

The results presented here are from static load and cyclic load fracture mechanics tests on carbon steel. They were performed to determine a threshold stress intensity for measurable crack propagation rates in simulated basalt repository groundwater. A companion study [3] investigated a possible influence upon EAC processes due to the radiolysis of groundwater by gamma irradiation.

Since the outside surface of the repository containers will come in contact with groundwater during the repository lifetime, it is necessary to characterize any EAC that could potentially occur. The simulated groundwater employed in this series of tests was of the Grande Ronde No. 4 (GR-4) composition, and nominal values for this composition are shown in Table 1. This water was further conditioned by contact with approximately 1-kg crushed basalt rock that was placed in the autoclave test chambers in close proximity to the test specimens. The crushed rock acted as an oxygen "getter" and dissolved oxygen levels in the water, as measured by the ASTM Test Method for Dissolved Oxygen in Water (D 888-81) colorimetric indigo carmine method, were approximately 5 ppb or less.

Fatigue crack propagation tests were conducted in an autoclave test system which allowed cyclic loadings to be applied to the specimen through a sliding seal penetration in the autoclave [4]. Groundwater recirculated throughout the system at a rate of approximately 80 mL/h. The autoclave pressure was 6.89 MPa, and test temperatures were 100, 150, and 250°C.

Crack lengths were inferred from compliance measurements throughout each test using an eddy current measurement system [4]. Crack growth rates per cycle (da/dN) were calculated using the "secant method" (see ASTM Test Method for Measurements of Fatigue Crack Growth Rates (E 647-86)), and stress intensity factor ranges (ΔK) were calculated using the standard formula also found in ASTM E 647-86. Linear elastic fracture mechanics (LEFM) validity was assured by use of a "flow stress criterion" [5], which limits plasticity in the remaining uncracked ligament.

Static load tests were conducted in an autoclave within which the groundwater was also conditioned by the inclusion of 1 kg of crushed basalt rock. Unlike the cyclic load tests, the groundwater was not recycled through the static load autoclave. Modified wedge-opening load (MWOL) specimens [6] were loaded in room temperature groundwater, and then transferred to the autoclave where the temperature was then increased to the appropriate test temperature. Test times were approximately 2000 and 20 000 h.

Results and Discussion

The results for the static load tests are summarized in Table 2. Results are shown for A36 steel and welds as well as for A27; A36 is the wrought equivalent of cast A27. Initial loads

Spec. No.	Material	Final K-Level, MPa √m	Exposure Time, h	Test Temperature, °C
2720	A27	28.9	2 000	150
2721	A27	34.0	2 000	150
2717	A27	39.9	2 000	150
2719	A27	25.7	2 160	250
2718	A27	30.9	2 160	250
2716	A27	40.2	2 160	250
2683	A36	29.4	2 180	150
2686	A36	37.8	2 180	150
2687	A36	47.6	2 180	150
2685	A36	26.8	2 000	250
2689	A36	33.0	2 000	250
2684	A36	40.0	2 000	250
2688	A36	27.4	20 000	250
2681	A36	36.8	20 000	250
2682	A36	40.8	20 000	250
2875	A36 weld	29.9	2 000	150
2876	A36 weld	40.1	2 000	150
2878	A36 weld	53.0	2 000	150
2874	A36 weld	25.8	2 160	250
2877	A36 weld	32.7	2 160	250
2873	A36 weld	45.9	2 160	250

TABLE 2—Summary of static-load tests in a groundwater environment.

applied to the specimens were slightly higher than the final loads shown in Table 2. The load drops were not the result of crack extension. They were instead due to two causes: a small time-independent plasticity associated load drop due to the yield strength difference between room and test temperatures, and a small time-dependent creep component. No crack extension was noted in any of the MWOL specimens shown in Table 2. This was verified two ways: post-test examination of the fracture surfaces following fracturing the specimens in liquid nitrogen, and by comparison of the pre-test and post-test compliances.

Fatigue crack propagation (FCP) tests were conducted in groundwater environments at temperatures of 100, 150, and 250°C, and the results are shown in Figs. 2 to 4, respectively. Also shown, for purposes of comparison, are the trend lines for A27 steel tested in air and vacuum environments under similar conditions. A number of observations may be made considering the results shown in Figs. 2 to 4. Firstly, at the lower values of ΔK , FCP rates in the groundwater are generally lower than in air. Eventually, however, FCP rates in the groundwater rise above those in air as ΔK increases. In a similar fashion, FCP rates in the groundwater generally fall close to, or below, rates in vacuo at the lower values of ΔK , and then rise above the vacuum rates as ΔK increases. Assuming that FCP rates in vacuo represent the basic mechanical component of fatigue crack extension, then this suggests that there is an effect of the groundwater environment relative to a vacuum. There are instances at both 100 and 150°C where FCP rates in the groundwater appear to be lower than those in vacuo. There is, of course, no physical rationale for such phenomena to actually occur, and it is far more likely that the results in groundwater are being influenced by crack closure processes at low ΔK . Significant amounts of corrosion products (and possible mineral deposits) have been observed on the fracture faces of specimens tested in the groundwater, and these could tend to wedge the crack open at low ΔK . It was not possible, within the present program scope, to quantify the depth of the deposits. If this could have been quantified, it is likely that the actual ΔK would be less than the measured ΔK , and the results in groundwater would therefore not appear to fall below those in vacuo.





FIG. 2—Fatigue crack propagation behavior of A27 steel in groundwater and air environments at 100°C.

Due to instrumentation difficulties, reliable compliance results were not obtained for three specimens (Specimens 2974A and 2975A in Fig. 3, and Specimen 2726 in Fig. 4). Hence average FCP rates are shown along with the range of ΔK over each specimen. Although the change in crack length (Δa) increments were generally larger than those suggested by ASTM E 647-86, useful information was still obtained from these specimens.

The tests conducted at 150 and 250°C represented several cyclic frequencies ranging over several orders of magnitude. It will be noted that at both temperatures, there is a general lack of dependence of FCP rates upon the cyclic frequency. This is in contrast to results [7] for a wrought carbon steel, ASTM A333-6, tested in oxygenated water over the temperature range 149 to 288°C where significant frequency effects were noted. The pH and dissolved oxygen levels of the Ref 7 water were 5.0 and 8 ppm, respectively, while those in the present



STRESS INTENSITY FACTOR RANGE, ΔK, ksiv in.

FIG. 3—Fatigue crack propagation behavior of A27 steel and HAZ weldment in a groundwater environment at 150°C.





study were 9.7 and <5 ppb, respectively. Although the exact mechanistic roles of these parameters is presently not completely understood, they clearly have an important influence upon FCP behavior.

Also shown in Fig. 3 for comparison purposes are data [8] for ASTM A216-WCA cast steel tested in deionized water at 150°C. This is essentially the same steel as the present ASTM A27, and although there is not a great deal of overlap, the agreement between the two data sets appears to be good.

Comparing the FCP curves of the present study for groundwater at 100, 150, and 250°C reveals that the behavior is essentially identical at 100°C and 250°C. On the other hand, FCP rates are slightly higher at 150°C, suggesting that a maximum occurs somewhere between 100 and 250°C. A similar maximum of 170 to 200°C is cited by Scott [9] for ASTM A302-B steel in low oxygen (0.05 to 0.2 ppm) deionized water. In contrast, at a given level of ΔK , the FCP rates of Ref 7 for ASTM A333 in oxygenated water increase progressively with temperature at 149, 232, and 288°C. Dissolved oxygen content apparently has a role in influencing both the absolute magnitude as well as the temperature dependency of FCP behavior in elevated temperature aqueous environments.

As discussed earlier, a test was also conducted where the crack propagated within the HAZ of a weldment in A27 steel (see Fig. 1). The results of this test are shown in Fig. 3, and it will be noted that FCP rates in the HAZ weldment are equivalent to, or slightly lower than, those in the cast A27 steel. This trend has been observed previously [10] for weldments in ferritic/pearlitic steels tested in air.

Tests were also conducted in 150°C groundwater to survey the effect of the stress ratio R ($R = K_{\min}/K_{\max}$) upon the FCP behavior. This is considered important since the anticipated repository loadings will correspond more closely to static (R = 1.0) conditions. The results, shown in Fig. 5, reveal the expected trend that, at a given value of ΔK , FCP rates increase with increasing R (on the basis of K_{\max} FCP rates decrease with increasing R). Also shown are estimates of the FCP behavior *in vacuo* at R = 0.5 and R = 0.75, based on the results of Ref 11.

It should be apparent from the foregoing discussion and figures that the GR-4 groundwater is a relatively nonaggressive environment in which to grow cracks. It is certainly less aggressive than the oxygenated water of Ref 7, and also less aggressive than typical light water reactor environments (see, for example, Ref 12).

The details of how the information from the cyclic and static load tests will be utilized to help assure the integrity of the nuclear waste container will be discussed next. Briefly, the cycle based growth rate da/dN is converted to a time-based rate da/dt, and ΔK is converted to K_{max} . The basic mechanical component of fatigue damage (that is, vacuum behavior) is then subtracted from the total measured growth rate to establish a component of the crack growth rate due to the environment. Since the vacuum and total measured growth curves intersect, this produces a point of "zero" environmental compart of growth, and this is taken to be a threshold for EAC. This "threshold" value of K is considerably lower than the maximum levels of K (for which no cracking was observed) in the static load tests shown in Table 2 (see also Refs 13–15).

This use of cyclic load results to establish a threshold for actual service loadings that are static is conservative. For example, the tentative "threshold" for EAC at 250°C established using cyclic loads was 15.7 MPa \sqrt{m} [16] while no cracking was observed in an A36 static MWOL specimen loaded to 40.8 MPa \sqrt{m} for 20 000 h (Table 1). Reference 16 then shows how the assumed "threshold" of 15.7 MPa \sqrt{m} is expressed in terms of a map of combinations of crack sizes and stress levels that should ensure that EAC will not compromise the container integrity.



STRESS INTENSITY FACTOR RANGE, AK, ksivin.

FIG. 5—The effect of stress ratio upon fatigue crack propagation behavior of A27 steel in a groundwater environment at 150°C.

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Corrosion Fatigue Cracking of Chromium-Containing Steels

REFERENCE: Harty, B. D. and Noël, R. E. J., "Corrosion Fatigue Cracking of Chromium-Containing Steels," *Environmentally Assisted Cracking: Science and Engineering, ASTM STP 1049*, W. B. Lisagor, T. W. Crooker, and B. N. Leis, Eds., American Society for Testing and Materials, Philadelphia, 1990, pp. 505–520.

ABSTRACT: Three chromium-containing steels, 3CR12, Alloy 825, and AISI 431, have been subjected to cyclic loading in air, distilled water, and low chloride containing waters. The 3CR12 steel showed significant fatigue crack growth rate (FCGR) enhancement when subjected to the aqueous environments. Fractography revealed the presence of isolated regions of intergranular and cleavage cracking that were correlated with plateaus observed on the FCGR curves. The Alloy 825 steel showed a FCGR enhancement in the aqueous environments but exhibited a decrease in FCGR with an increase in chloride content. The fracture was observed to be a mixed mode, that is, intergranular separation and transgranular cleavage. The AISI 431 stainless steel exhibited a FCGR enhancement and a low density of widely distributed intergranular features when tested in distilled water; in the chloride-containing environments, the FCGRs decreased progressively with respect to the air data. The corrosion fatigue behavior of the three steels has been discussed in terms of dissolution and hydrogen-assisted cracking.

KEY WORDS: corrosion fatigue, chromium, steels, chloride, fatigue (materials), crack growth rate, aqueous environments, fractography, intergranular cracking, cleavage, fracture mode, dissolution, hydrogen-assisted cracking, environmental effects, cracking

The environmental conditions in South African gold mines are extremely harsh. Materials of construction have to withstand abrasive quartzitic rock and mine waters that contain chlorides, sulfates, nitrates, and dissolved oxygen. These waters are often acidic and lead to the rapid corrosion of both mild steels and proprietary abrasion resistant steels. In view of these aggressive conditions, the Chamber of Mines Research Organization has initiated a research program in order to "design" steels with a sufficient combination of both abrasive and corrosive wear resistance. Furthermore, these steels are required to have acceptable fabrication properties and weldability. Several candidate steels have been developed and their abrasive-corrosive properties have been recently discussed [1,2].

The use of these steels in mining machinery will expose them to both stress corrosion and corrosion fatigue attack. This paper reports the results of the initial investigation of the corrosion fatigue cracking susceptibility of one of the newly developed steels (Alloy 825)³ with respect to a relatively new corrosion resistant steel (3CR12) and a proprietary stainless steel (AISI 431).

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³ In this instance, Alloy 825 refers to a quenched and tempered chromium-containing steel and should not be confused with the North American nickel-based alloy of the same name.

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Material	С	Mn	Si	Мо	Cr	Ni	Ti	S
3CR12	0.026	1.138	0.48	0.04	11.27	0.60	0.17	0.012
Alloy 825 AISI 431	$0.250 \\ 0.200$	$\begin{array}{c} 0.020\\ 0.400 \end{array}$	$\begin{array}{c} 0.03 \\ 0.300 \end{array}$	0.01	$\begin{array}{c} 8.00\\ 16.50\end{array}$	$\begin{array}{c} 3.00 \\ 1.80 \end{array}$	···· ···	0.300

TABLE 1—Typical chemical compositions of the test materials.

Experimental

Materials

The typical compositions of the three chromium-containing steels are listed in Table 1. The 3CR12 steel was tested in the hot-rolled, annealed condition; the Alloy 825 was soaked at 1100°C (2012°F) for 1 h, oil quenched, and tempered at 200°C (392°F); and the AISI 431 was marquenched from 1040°C (1904°F) to 175°C (347°F) before undergoing an air quench followed by a double temper at 260°C (500°F). The predominant phases present within the microstructures and some mechanical properties of the steels are listed in Table 2. The Alloy 825 contains small amounts of retained austenite distributed as thin films around the martensite laths.

Procedure

Fatigue crack growth rate (FCGR) tests were carried out in accordance with ASTM Test Method for Constant-Load-Amplitude Fatigue Crack Growth Rates Above 10^{-8} m/Cycle (E 647-83) (1980) using a servo-hydraulic mechanical testing machine. Experiments utilized 25-mm-thick compact tension specimens with a longitudinal-transverse orientation. All tests were conducted using tension-tension, sinusoidal cyclic loading with a load ratio, R = 0.1, and a load range, $\Delta P = 14.4$ kN. Tests performed in air were carried out at a frequency of 3 Hz, and all tests in aqueous environments were conducted at 1 Hz. The aqueous test environment was contained around the specimen in a polymethyl methacrylate corrosion cell that was continuously replenished from a thermally controlled reservoir. A recirculation rate of approximately 630 mL/min and a temperature of 25°C (77°F) were maintained throughout testing. Crack length was monitored via a data acquisition and computer system using the back face strain technique [3,4].

Environmentally assisted crack growth rate testing was undertaken in three different environments: distilled water, water containing 500 ppm chloride (500 ppm Cl⁻), and water containing 1000 ppm chloride (1000 ppm Cl⁻). Most tests were performed at the free corrosion potential; a number of tests were carried out with the specimens held at -1200

Material	Microstructure	Approximate Grain Size, µm	Hardness, VHN30	Yield Strength, MPa	Tensile Strength, MPa
3CR12	dual phase ferrite/ martensite	25	167	380	530
Alloy 825	dual phase martensite/	80	540	1200	1710
AISI 431	martensite	50	449	1200	1480

TABLE 2—Microstructures and some mechanical properties of the test materials.

mV saturated calomel electrode (SCE) in the 1000 ppm Cl⁻ solution (indicated as -1200 mV in the legends of the FCGR curves). Crack length measurements were collected approximately every 0.25 mm and, at the conclusion of the experiment, were corrected for crack curvature before processing with a seven-point polynomial data reduction program to determine the crack growth rate (da/dN) as a function of the stress intensity factor range (ΔK) .

Fracture surfaces were examined using scanning electron microscopy (SEM), and topographical features were recorded.

Experimental Results

Tests in Air

A graph depicting the fatigue behavior of the three materials tested in air at a frequency of 3 Hz is presented in Fig. 1. The dual phase 3CR12, consisting of ferrite and low-carbon lath martensite, clearly exhibits greater fatigue resistance in air than the medium-carbon martensitic steels, Alloy 825 and AISI 431. Characteristic Stage II linear behavior [5] was observed for both 3CR12 and AISI 431 that cracked transgranularly by the mechanism of reversed plastic slip [6] (Figs. 2 and 3, respectively). Because of the many available slip systems in these body-centered cubic metals, striations are not always clearly visible but the mechanism may still be referred to as a striation mechanism. Although the fracture mode for Alloy 825 was predominantly striation, sufficient intergranular separation had occurred to influence the macrocrack growth rates. The deviations from linear behavior in the FCGR curve for this alloy coincide with a finely distributed formation of intergranular facets on the fracture surface (Fig. 4). A small number of cleavage-type features were observed on the AISI 431 fracture surface (Fig. 5). These regions were found to be a relatively soft delta ferrite phase and appeared to have no effect on the macrocrack growth rate behavior shown in Fig. 1.

Tests in Aqueous Environments

3CR12—The FCGR properties of 3CR12 tested in air and at free corrosion potentials in distilled water, 500 ppm Cl⁻ solution, and 1000 ppm Cl⁻ solution are shown in Fig. 6. In addition, the data obtained from a specimen held at -1200 mV (SCE) in 1000 ppm Cl⁻ solution is shown. The air data, although obtained at a different frequency to the environmental cracking data, are used as a reference since, broadly speaking, laboratory air may be considered to constitute an inert environment in which the frequency of cyclic loading has no effect on FCGRs. Similar fatigue crack growth rates (FCGRs) were obtained between stress intensities of about 15 and 25 MN m^{-3/2} for the aqueous environmental tests. Differences in relative performance are seen above and below those values of stress intensity.

The FCGR curves obtained in the aqueous environments feature a number of "plateaus" that were correlated with cleavage or intergranular features observed on the fracture surfaces of the specimens at the corresponding distances calculated from the stress intensity values. It was noted that the plateaus that occur at relatively low stress intensity factors could be attributed to intergranular features on the fracture surfaces (Fig. 7) while those at higher stress intensity factors could be attributed to cleavage features (Fig. 8). These topographical features and plateaus were not observed for the 3CR12 tested in air. No additional FCGR effects were exhibited by the specimen held at -1200 mV (SCE) in the 1000 ppm Cl-solution.


FIG. 1—The FCGR behavior of the materials tested in air at a frequency of 3 Hz.



FIG. 2—General fracture appearance of 3CR12 tested in air at 3 Hz; $\Delta K = 30 MN m^{-3/2}$. (Note: arrow indicates direction of cracking and is the same for all fractographs.)



FIG. 3—General fracture appearance of AISI 431 tested in air at 3 Hz; $\Delta K = 36 MN m^{-3/2}$.



FIG. 4—Intergranular facets on the surface of Alloy 825 tested in air at 3 Hz; $\Delta K = 16 MN m^{-3/2}$.



FIG. 5—Fracture appearance of AISI 431 tested in air showing cleaved delta ferrite region; $\Delta K = 16 MN m^{-3/2}$.



FIG. 6—Influence of environment on the rate of crack growth of 3CR12.



FIG. 7—Intergranular cracking on 3CR12 surface tested in 1000 ppm Cl⁻ solution; $\Delta K = 21 \text{ MN m}^{-3/2}$.



FIG. 8—Cleavage on 3CR12 surface tested in 500 ppm Cl⁻ solution; $\Delta K = 40 \text{ MN m}^{-3/2}$.

Alloy 825—The FCGRs of Alloy 825 were significantly greater in the aqueous environments than in air, and the alloy showed a decrease of FCGR with an increase in chloride content of the aqueous environment (Fig. 9). The environmentally induced fracture was observed to be mixed mode, that is, intergranular separation and transgranular cleavage (Fig. 10). The striation mechanism generally observed for Alloy 825 after tests in air was not observed for specimens tested in any of the aqueous environments. Corrosion therefore plays a significant role in the fatigue fracture process. The specimens tested in the 500 ppm Cl^- solution and distilled water showed significantly more transgranular cleavage than those tested in 1000 ppm Cl^- solutions. The SEM investigations of the specimen tested in 500 ppm Cl^- solution showed that plateaus on the FCGR curves occurred at points on the fracture surface where the ratio of intergranular to cleavage cracking increased.

A corrosion product deposit was evident over the whole fracture surface at the end of the test for all aqueous conditions. A thicker layer of corrosion product obscured the fracture surfaces in an area near the initial notch and was considered to be the result of reactions occurring behind the propagating crack front. No significant difference in FCGR behavior and fracture surface appearance was observed for the two tests performed in the 1000 ppm Cl^- solutions (rest potential and -1200 mV (SCE)); similarly no significant difference between the 500 ppm Cl^- and distilled water tests was observed.

AISI 431—The test conducted in distilled water showed an increase in FCGR with respect to the air data (Fig. 11). A small amount of corrosion product was observed on the fracture surface and a change in cracking mechanism was evident. This was revealed by SEM as intergranular features on a predominantly transgranular striation background (Fig. 12).

The results obtained for tests in the aqueous environments (Fig. 11) exhibited a decrease in FCGR with an increase in the chloride content of the solutions. Moreover, there was a decrease in the FCGRs for the chloride solution tests with respect to the air fatigue data. No plateaus were observed on the FCGR curves. The fracture surfaces of the specimens tested in the chloride solutions exhibited a similar striation mechanism to that for the specimen tested in air. However, there was a dense layer of corrosion product on these fracture surfaces.

Discussion

The FCGRs are a function of the microstructure, chemical composition, and mechanical properties of the steels. The greater fatigue resistance shown by 3CR12 in air with respect to the other two steels occurs by virtue of its fine dual-phase microstructure consisting of ferrite grains and regions of low-carbon lath martensite that confers good ductility and toughness.

The environmental effects on the steels have resulted in either an acceleration or retardation of the FCGRs with respect to the air data. In aqueous environments, corrosion processes at the tip of a crack have been shown to contribute to crack extension on the rising tensile ramp of a fatigue cycle for a 12Ni-5Cr-3Mo maraging steel [7]; on tensile opening, the deformation at the crack tip ruptures the protective oxide film exposing fresh metal to the local environment. Until repassivation occurs, two factors can influence the FCGRs at that point; either (1) anodic dissolution or (2) hydrogen embrittlement, better referred to as hydrogen-assisted cracking (HAC), arising from hydrogen ingress into the steel.

Slow or zero passivation rates following oxide rupture at the crack tip can lead to excessive dissolution of the freshly exposed and strained metal resulting in crack blunting and even crack arrest under given load conditions [8]. If corrosion product is retained in the crack,



FIG. 9—Influence of environment on the rate of crack growth of Alloy 825. (Note: the broken line indicates a disruption during testing.)



FIG. 10—Mixed-mode cracking on Alloy 825 surface tested in 500 ppm Cl⁻ solution: (a) $\Delta K = 30$, and (b) $\Delta K = 35$ MN m^{-3/2}.



FIG. 11—Influence of environment on the rate of crack growth of AISI 431.



FIG. 12—Interganular features on AISI 431 surface tested in distilled water: (a) $\Delta K = 19$, and (b) $\Delta K = 35 \text{ MN m}^{-3/2}$.

the increased volume of the product over that of the metal from which it has been formed, may lead to oxide-induced closure [9]. This would result in a decrease of the effective stress intensity factor and a decrease in FCGRs.

Accompanying the dissolution reaction at the crack tip are two possible cathodic reactions: the reduction of dissolved oxygen to hydroxyl ions and the reduction of hydrogen ions to atomic hydrogen [10]. A review by Congleton and Craig shows that the pH within a crack is generally lower than that of the bulk solution [11]. The acidic conditions would tend to favor the hydrogen ion reduction reaction. The atomic hydrogen is adsorbed onto the metal surface and may diffuse into the metal lattice. Its presence affects the integrity of the metal making it susceptible to cracking at lower load conditions.

In summary, the deformation at a crack tip in an aggressive environment can result in enhanced FCGRs by localized dissolution, or decreased FCGRs due to crack blunting or oxide-induced closure. Alternatively, adsorption of hydrogen at local cathodes may lead to HAC and consequent acceleration of crack growth. These possible mechanisms are in competition and the dominant mechanism will be that with the greatest overall kinetics. The results for tests in aqueous environments will be discussed in terms of these possibilities.

The 3CR12 steel showed a predominant striation cracking mode when tested in the aqueous environments. The fracture surfaces had a rougher appearance than the surface of the specimen tested in air. The FCGRs obtained from the aqueous tests showed a general increase with respect to the air data. It is obvious that the environment enhanced the cracking process although the mode of cracking remained the same until, at a number of stress intensity ranges, the fracture surfaces showed isolated areas of cleavage or intergranular separation corresponding to the plateaus on the rate curve in Fig. 6. The high initial FCGR obtained for 3CR12 in distilled water could not be correlated with any unusual features on the fracture surface.

The occurrence of the isolated intergranular and cleavage features at low and high stress intensity ranges, respectively, for 3CR12 is in accord with results obtained by Beachem [12]. He suggested that, for HAC, intergranular cracking was a lower energy process than cleavage; furthermore, the lower FCGRs encountered at the lower stress intensity ranges may permit hydrogen diffusion further ahead of the crack tip, permitting hydrogen concentration at the grain boundaries and making the conditions for grain boundary separation more favorable. The greater strain rates experienced at higher stress intensity ranges would, in contrast, favor cleavage.

The incidences of transient mechanistic changes exhibited by 3CR12 imply that there are critical conditions required to trigger the onset of HAC and that these conditions have been attained only in isolated regions; critical factors are the local crack tip chemistry and mechanical conditions. It is believed that the FCGRs of 3CR12 in the aqueous solutions have been generally enhanced by a dissolution mechanism and that critical conditions for HAC have been attained in isolated regions resulting in the transient domination of this mechanism. It is generally accepted that HAC often occurs in high-strength alloy steels, such as Alloy 825, when exposed to aqueous environments; it manifests itself in the form of intergranular or cleavage cracking [13,14]. This suggests that HAC is the dominant mechanism in the environmentally assisted cracking of Alloy 825.

The FCGR data and the SEM fracture study show that for Alloy 825 an increasing amount of transgranular cleavage corresponds to an increase in FCGRs. This result is in agreement with Beachem's model on HAC [12] linking faster crack growth rates with cleavage processes.

It has been stated previously that hydrogen atoms may be adsorbed at local cathodic sites and may lead to HAC. If these cathodic sites are obstructed, for example, by corrosion product from reactions within the crack, the process of hydrogen adsorption, and therefore the effect of the hydrogen on the integrity of the material, will be diminished [15]. Consequently, an expected higher corrosion rate in the 1000 ppm Cl⁻ solutions than in the other aqueous solutions would give rise to an increase in the amount of corrosion product in the crack. A visible increase in the corrosion product for tests conducted in 1000 ppm Cl⁻ solutions was in fact observed, thus resulting in either a decrease in the effects of hydrogen or oxide-induced closure that would reduce FCGRs with respect to those obtained in the less aggressive aqueous environments. The fact that the test conducted at -1200 mV (SCE) showed no significant increase in FCGRs with respect to the other aqueous tests suggests that the specimen might not have been entirely polarized even though the potentiostat was set at -1200 mV (SCE).

The test performed on AISI 431 in distilled water resulted in increased FCGRs with respect to air. The fracture surface was similar to that for the specimen tested in air but showed small, visible quantities of a corrosion product and a low density of widely distributed intergranular features (Fig. 12). The small number of intergranular features suggests that some HAC was able to take place; however, it is believed that the dissolution mechanism was dominant.

Large amounts of visible corrosion product resulted from the tests on AISI 431 stainless steel in the chloride solutions although the underlying fracture surfaces were similar to that of the specimen tested in air; no evidence for HAC was observed. This suggests that the dissolution mechanism plays a dominant role in the environmentally assisted cracking (EAC) of AISI 431 in these chloride solutions. If the air conditions can be assumed to be inert, the lower FCGRs exhibited by AISI 431 in the chloride solutions must be explained by crack blunting or oxide-induced closure. The corrosion product from the dissolution mechanism would also serve to block local cathodic sites, reducing the possibility of HAC.

It is apparent that the occurrence of HAC as a dominant mechanism in the EAC of the three steels has decreased from showing a large dominance in Alloy 825 to being transient in 3CR12 and barely significant in AISI 431. No attempt will be made to compare the relative environmental behavior since the three steels differ greatly in their microstructure, chemical contents, and mechanical properties.

Conclusions

The mechanisms by which EAC has occurred have varied for each alloy, and the degree of FCGR enhancement or retardation has differed with the environment.

- 1. The 3CR12 showed significant FCGR increases when tested in the aqueous environment. Isolated regions of cleavage and intergranular cracking were observed.
- 2. The Alloy 825 showed significant FCGR increases when subjected to the aqueous environments as well as a trend in which the FCGRs decreased with an increase in the chloride content of the solutions. The fracture mode was completely transformed in the aqueous environments.
- 3. The trend of decreasing FCGRs with an increase in chloride content of the aqueous solutions was also exhibited by AISI 431. The FCGRs obtained in the chloride solutions were below those obtained in air. A low density of widely distributed intergranular features was observed on the fracture surfaces of the specimen tested in distilled water.
- The imposed potential of −1200 mV (SCE) on the 3CR12 and Alloy 825 specimens in 1000 ppm Cl⁻ solution had no additional effect on respective cracking mechanisms or FCGRs.

Acknowledgment

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Evaluation of Cavitation-Erosion Resistance of Ion-Plated Titanium Nitride Coating

REFERENCE: Matsumura, M., Oka, Y., Ebara, R., Kobayashi, T., Odohira, T., Wada, T., and Hatano, M., "**Evaluation of Cavitation-Erosion Resistance of Ion-Plated Titanium Nitride Coating**," *Environmentally Assisted Cracking: Science and Engineering, ASTM STP 1049*, W. B. Lisagor, T. W. Crooker, and B. N. Leis, Eds., American Society for Testing and Materials, Philadelphia, 1990, pp. 521–533.

ABSTRACT: Cavitation-erosion tests of steel, coated with a layer of titanium nitride (TiN) by physical vapor deposition, were conducted using a wall-facing vibratory testing facility and an ultrasonic cavitation-erosion testing facility based on the ASTM Method for Vibratory Cavitation Erosion Test (G 32-85). The amount of erosion damage to the test specimen was evaluated by various methods. It was confirmed that the erosion resistance of TiN coated steel is superior to steel coated with the same film thickness of electroplated chromium, and of course to uncoated base metal (SUS410J1 stainless steel). It has been also confirmed that chromium-titanium nitride multilayered coating shows the most effective erosion resistance among the tested ion-plated coating specimens. The reasons of this improvement in the erosion resistance of TiN coated materials are as follows. First, the TiN layer did not peel off from the substrate surface, owing to its adhesion strength. Secondly, the erosion resistance of the layer itself was greater than that of the substrate material. In addition, it has been confirmed that this erosion resistance is maintained even after the erosion damage has reached the substrate material, since the residual stress generated by the layer deposition improves the durability of the base metal.

KEY WORDS: environmental effects, ion-plated Cr-TiN coating, cavitation erosion, wallfacing vibratory test, vibratory test, stainless steels, residual stress

Recently, ceramic-coated materials have been receiving attention. The ceramic coating is applied to the substrate material by new techniques, such as chemical vapor deposition (CVD), or physical vapor deposition (PVD), the latter method being more precise than the former. By applying one of these methods, a coating of only a few micrometres produces excellent wear resistance, which makes it possible to protect the surface without decreasing the accuracy of measurement of the base metal. Based on these methods, we attempted to

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use PVD ceramic-coated material to prevent cavitation-erosion of structural materials in industrial precision machinery.

There has been much research done on ceramic-coated materials deposited by the ionplating technique; for example, the effects of various factors on forming the coatings [I], the characteristics of the coatings [2,3], and the residual stress generated in the coatings [4,5]. However, there have been few reports on the fracture characteristics of the coating, except for the report on the effects caused by substrate bias voltage/introduction pressure on the wear resistance [6]. Both the evaluation of the erosion resistance of ceramic-coated materials, and the fracture behavior of the material have not been fully studied. Therefore, in this paper, we describe the cavitation-erosion resistance of martensitic stainless steel which was ion-plated with titanium nitride (TiN), a ceramic-coating material in comparison with other coating materials, using wall-facing vibrator and vibratory cavitation-erosion testing facilities. From the results of these cavitation-erosion tests, we compared and evaluated these two methods of testing. We also describe how coating improves the erosion resistance of the substrate material.

Experimental Procedure

The base metal was martensitic stainless steel SUS410J1 (JIS G 4303). The test specimen is illustrated in Fig. 1. The surface was polished with emery paper up to No. 1500. Table 1 illustrates the chemical composition and mechanical properties of the base metal. The polished base metal was ion-plated with TiN at a nitrogen introduction pressure of 6.0×10^{-2} Pa and a temperature of 773 K. In order to evaluate the erosion resistance, electroplated chromium, ion-plated chromium, ion-plated chromium nitride (CrN), and Stellite (bulk) were used as controls. The compositions of the coating materials are shown in Table 2. In this table, TiN IP indicates the titanium nitride ion-plated material, and CrEP is the chromium electroplated material. Four types of multilayered chromium-titanium nitride (Cr-TiN) coatings, whose bias conditions varied from 0 to 130 V, were deposited at a constant substrate temperature of 773 K. The bias conditions and the thickness of these coatings are shown in Table 3.

X-ray diffraction analysis was carried out to determine the residual stress in the coatings. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy were used to observe the microstructure of the coatings. The scratch test, using an acoustic emission sensor to determine the critical load, was used to evaluate the adhesion behavior of the coatings.



FIG. 1—Test specimen, unit = mm.

ase Metal SUS410J1.ª
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properties (
mechanical
and
1-Chemical compositions
TABLE

	Brinell Hardness, HB	217	
cal Properties	Charpy 2 mm U-Notch, Impact Value, N · m/cm ²	262.6	
	Reduction of Area,	68.2	ir-cooled.
Mechani	Elongation, 50 mm, %	27.3	tor 3 h and a
	Tensile Strength, MPa	735	red at 983 K
	Yield Strength 0.2% Offset, MPa	570.3	ched, tempe
	Fe	bal.	-duenc
	Mo	0.36	nin, oil
%	ර	12.10	K for 45 1
sitions,	ïz	0.49	1243
Chemical Compo	s	0.003	itized at
		0.022	s austen
	Mn	0.49	erial wa
	<u></u>	0.38	he mate
	C D	0.13	Ľ,

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Material	Thickness, µm	Hardness, H _{v0.05}	
CrEP ^a	10	570	
CrEP	20	570	
Cr IP ^b	12	441	
TiN IP	3.5	1880	
TiN IP	12	1880	
Cr-CrN IP	18 (Cr:13, CrN:5)	1290	
Cr-TiN IP	15.5 (Cr:13, TiN:2.5)	1530	
Stellite (bulk)		593	

TABLE 2—Coating materials.

^{*a*} EP = electroplated.

^b IP = Ion plated.

As a cavitation generator, a wall-facing vibratory cavitation-erosion testing facility [7], as illustrated in Fig. 2, was used. The test specimen was fixed to the base of the apparatus that allowed slight upward/downward movement. The specimen was located 0.4 mm from the vibratory nozzle that was set on the tip of the horn. The nozzle vibrated vertically at a frequency of 19.9 kHz with an amplitude of 25 μ m. The testing liquid (deionized water) was forced through the core of the horn and allowed to radiate out from the center of the vibratory nozzle onto the test surface. In this method, as the horn is cooled by the testing liquid, no dilation of the horn occurs; hence, the gap between the test specimen and the vibratory nozzle was kept constant during the testing procedures. In turn, the cavitation impact pressure generated on the test surface was also kept constant; thus, the reproducibility of the test results was improved extensively. The temperature of the testing liquid was maintained at 313 K by a heater.

Further tests of the cavitation-erosion were conducted based upon the ASTM Method for Vibratory Cavitation Erosion Test (G 32-85) using the specimen shown in Fig. 1 to compare the results of wall-facing vibratory tests from the viewpoint of evaluation of cavitation-erosion acceleration. The testing facility is schematically illustrated in Fig. 3. The frequency employed during the testing was 18.3 kHz, and the amplitude at the tip of the specimen was 40 μ m. The temperature of the deionized water was kept constant at 290 K. The reason why two different types of cavitation-erosion facilities were used will be discussed later.

Results and Discussion

Evaluation of Cavitation-Erosion Resistance of Coatings

Figure 4 shows the cumulative weight loss of the test specimens of various coated materials including the base metal (SUS410J1 steel) obtained in the wall-facing vibratory test. In this

No.	Thickness		Bias Voltage		Critical Land
	Cr (µm)	 TiN (μm)	Cr (V)	TiN (V)	N
1	8.4	3.4	0	0	12
2	8.8	4.1	0	130	16
3	4.3	3.5	130	0	8
4	3.3	4.0	130	130	11

TABLE 3—Critical loads of Cr-TiN multilayer coatings.



FIG. 2—Schematic diagram of wall-facing vibratory testing facility.

figure, TiN indicates the TiN ion-plated material, CrEP is the chromium electroplated material, and their corresponding numbers indicate the thickness of the coating. Upon initiation of the testing, an incubation period (during which no weight loss occurs) was followed by a weight loss period. The speed of this latter period increases gradually, which is typical of cavitation-erosion behavior of metallic materials [8]. In coated materials, a similar period, during which no weight loss occurred, was observed, but this period is viewed as the damage period of the coated layer and will be described in detail in the following section.

The weight loss of each specimen within an identical time period was compared. The weight loss of the coated materials was shown to be smaller than the weight loss of the uncoated materials, indicating that cavitation-erosion resistance is improved by the coating. Furthermore, when the same coating material was used, a thicker coating produced a higher erosion resistance. When the thickness of the coating was the same, the erosion resistance



FIG. 3-Schematic diagram of vibratory testing facility.



FIG. 4—Cumulative weight loss versus testing time for base metal (SUS410J1 stainless steel) and various coated metals (frequency = 19.9 kHz, amplitude = $25 \mu m$, and deionized water = 313 K). In this figure, TiNIP indicates the titanium nitride ion-plated material, CrEP is the chromium electroplated material, and their corresponding numbers indicate the thickness of the coating.

of the TiN deposited material was superior to that of the CrEP deposited material. In TiN10, the resistance was much higher than that of the other test materials. This suggests that ionplated TiN is an effective material for erosion resistance.

Figure 5 indicates the weight loss that occurred with time in the test specimens of various ion-plated materials during the wall-facing vibratory test and the vibratory cavitation-erosion test. As can be seen from the figure, the results of the tests do not show a large variance. The orders of merit of the materials tested are coincident with each other. In both tests the thicker the TiN layer, especially when it was applied as a multilayered coating, the higher



FIG. 5—Cavitation-erosion test results of ion-plated coatings (vibratory test and wall-facing vibratory test, TiN (10 µm, 1) = single coating and TiN (10 µm, 3) = triple coating).



FIG. 6—Cavitation-erosion test results of ion-plated multilayered coatings (frequency = 18.3 kHz, amplitude = $40 \mu m$, deionized water, 290 K).

was the erosion resistance. The results also indicate that ion-plated chromium produced a higher amount of erosion resistance than the electroplated chromium.

Thus, it has been confirmed that the vibratory test can be used for evaluating the resistance of coatings against cavitation erosion, and it has also an advantage in getting the test results quickly. The optimum condition for obtaining the most resistive coating, therefore, were searched for by using the facility of this type.

Figure 6 illustrates the cumulative weight loss with time in various multilayered ion-plated materials, as observed during the vibratory cavitation-erosion test [9]. The results suggest that the Cr-TiN multilayered coating produces the greatest erosion resistance.

Exfoliation Behavior of the Coating

In order to thoroughly study the exfoliation behavior of the coating, the surface of the test specimen of the wall-facing vibratory cavitation-erosion test was examined by SEM. This is because the specimen suffers no influence of vibratory acceleration, and it is expected to simulate field conditions more closely. As an example, Fig. 7 indicates an increase in the size of a flaw generated on the surface of the TiN10 test specimen during the coating process. From these micrographs, we can explain the exfoliation behavior of the coating as follows. As can be seen from the schematic section of a specimen as illustrated in Fig. 8, it is conceivable that the exfoliation proceeded through the following three stages.

- 1. The flaws generated during the coating process induced cavitations that do not widen significantly, but gradually increase in depth and reach the substrate metal (A-C).
- 2. A shell-shaped exfoliation then occurred around the edge of the cavity (D).
- 3. Finally, the shell-shaped portions scaled off in flakes and the exfoliated area expanded (E-G).

By measuring the exfoliated area by optical microscopy, it was revealed that during Stage 1, as outlined previously, only the coating was damaged. A study of the change in the depth of the surface flaw indicated that the depth increased almost linearly with respect to time







FIG. 8—Schematic illustration of a pit growing on 10 µm TiN-coated steel.

until the cavity reached the surface of the base metal. The slope of this resulting line was quite small compared to that of the base metal or uncoated metals. The aforementioned exfoliation of the coating will also occur in an area that does not contain a flaw once a flaw is generated in the coating as a result of an incubation period. The process will then proceed in the same manner as outlined previously.

The Causes of Erosion Resistance Improvement

(a) The Adhesive Strength of the Coatings—As mentioned in the previous section, flaws on the surface of the coating will eventually become cavities that deepen into pits. This causes the coating to exfoliate around the pits in flakes of several micrometres in thickness. This suggests to some extent, that the coated layer adheres firmly to the base metal so that complete exfoliation of the coating from the interface does not occur. Therefore, the improvement in erosion resistance could be a result of both the adhesive strength and the hardness of the coating itself. These observations were similar for TiN3.5 or chromium electroplated materials. Thus, the adhesive strength of these coatings is considered to be strong, to a certain degree. It is clear that the adhesive strength of the abovementioned materials is stronger than the destructive power caused by cavitation erosion under the testing conditions.

The adhesive strength of the ion-plated coating is influenced mainly by the substrate temperature and the bias voltage [10]. However, since the substrate temperature was kept constant (773 K) in this test, we deposited four types of multilayered coating materials whose bias conditions varied. We then studied their adhesive strength by way of the scratch test. The results of this test are shown in Table 3, while the results of the vibratory cavitation-erosion test are illustrated in Fig. 9. Table 3 and Fig. 9 suggest that the erosion resistance and adhesive strength are correlated. Sample 2, whose adhesive strength was the strongest, had the highest erosion resistance. This sample received a bias voltage during the deposition of the TiN topcoat.

Figure 10 indicates the result of the TEM observation and EDS analysis at the interface between ion-plated chromium and TiN layer of Cr-TiN multilayer coating deposited under a bias voltage during the deposition of TiN top coat [9] that were performed to study the effect of the substrate bias voltage. As shown in this figure, the interface between chromium and TiN layer exhibited a sound state of bonding. At the same time, the titanium atom penetrated the outer layer of chromium. The bias voltage, along with the titanium atom penetration are considered to be the main reasons for the strong adherence of the coating.

(b) Residual Stress of the Coating—As mentioned earlier, the damage rate of the coating within the base metal is smaller than that in the uncoated materials. This means that by applying a coating layer, the erosion resistance of the base metal itself was also improved. The residual stress generated during the coating process could be ascribed to this phenom-



FIG. 9—Cavitation-erosion test results of (Cr-TiN) coatings (frequency = 18.4 kHz and amplitude = $25 \ \mu m$).

enon. Therefore, we conducted a damage rate test after the TiN coated materials were tempered to release the residual stress. As shown in Fig. 11, it was ascertained that by tempering (1023 K for 3 h in vacuum and furnace cooled), the damage rate (the slope of the straight line prior to 11 h; arrowed in Fig. 11) of the coating was not changed, but the slope of the line of the base metal accelerated and corresponded to that of the uncoated material. On the other hand, measurement of the exfoliated area showed little change after heat treatment. This suggests that, due to the heat treatment process, the cavitation-erosion resistance of the coating itself did not change, while the resistance of the base metal changed to equal those of the uncoated materials. The fact that the damage rate changes due to the existence of residual stress that was generated within the material is apparent, as demonstrated by Matsumura et al. [7].

They reported that in the damage rate test of the metal materials on which a tensile load is added, the incubation period becomes prolonged. In other words, the amount of damage is suppressed, but the damage rate is accelerated. However, in the correlation of the damage rate and the residual stress, many factors related to the former are indicated, while the details of the effect of the residual stress remain to be proven.

Figure 12 indicates that heat treatment to the material releases the residual compressive stress of the base metal. To measure the residual stress, we employed a $2\theta \cdot \sin^2 \psi$ method [4] applying X-ray diffraction. This figure illustrates the comparison of the residual stress in the TiN layer and the base metal around the surface of the TiN coated materials before and after heat treatment. By coating, the base metal gained tensile stress and the residual compressive stress of the base metal itself was released. Although the residual compressive stress in the TiN layer did not change even after heat treatment, the same stress in the base







FIG. 11—Effect of heat treatment on growth rate of pit depth for 10 μ m TiN coating (frequency = 19.9 kHz, amplitude = 25 μ m, and arrow shows the point of 11 h).

metal nearly disappeared in the test specimen, TiN3.5. The residual stress of the base metal in the specimen TiN10 could not be measured since the absorption of the reflected X-ray from the coating was substantial. In this specimen, however, it is conceivable that the residual stress was nonetheless released by heat treatment just as in the TiN3.5 specimen. From these results, it is apparent that the improvement in the erosion resistance of the base metal was caused by the residual stress compressive generated during the coating process.



FIG. 12—Effect of heat treatment on residual stress for TiN-coated steel.

Conclusions

We conducted cavitation-erosion tests on TiN ion-plated material and uncoated (control) material and ascertained that the erosion resistance of each coated material was increased by the existence of the coating. We then looked at several reasons for the improvement in the erosion resistance. The results are as follows:

- 1. The vibrating cavitation-erosion test can be used for evaluating the resistance of coatings against cavitation erosion, and it also has an advantage in getting the test results quickly.
- 2. Since TiN ion-plated materials have a high degree of hardness, for comparable coating thickness, their erosion resistance is quite superior to that of the chromium electroplated materials. The thicker the coating is on the base material, the more erosion-resistant the material will become up to a thickness of 10 µm.
- 3. As compared to a single-layer coating of TiN, a multilayered coating of Cr-TiN shows higher erosion resistance.
- 4. The coating exfoliates first, followed by the base metal.
- 5. When a hard coating material is applied to a base metal, the time it takes the cavitation damage to reach the base metal is prolonged, which, in turn, improves the erosion resistance of the coated material. A significant factor of this erosion resistance is the adhesive strength of the coating to the base metal. Also, the residual compressive stress generated during the coating process suppresses the damage that occurs within the base metal.

In addition to the abovementioned points, it was demonstrated that the multilayered coating acts to improve erosion resistance. This indicates that some other factors related to the multilayering of the coatings may play a role in the erosion resistance. This latter point must be put to further study before it can be confirmed.

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