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intergranular corrosion of stainless alloys

R. F. Steigerwald, *editor*

american society for testing and materials

INTERGRANULAR CORROSION OF STAINLESS ALLOYS

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Foreword

This publication, *Intergranular Corrosion of Stainless Alloys,* contains papers presented at the Symposium on Evaluation Criteria for Determining the Susceptibility of Stainless Steels to Intergranular Corrosion which was held in Toronto, Canada, 2-3 May 1977. The symposium was sponsored by Committee A-1 on Steel, Stainless Steel, and Related Alloys and G-1 on Corrosion of Metals, American Society for Testing and Materials. R. F. Steigerwald, Climax Molybdenum Company, presided as symposium chairman and editor of this publication.

Related ASTM Publications

Localized Corrosion—Cause of Metal Failure, STP 516 (1972), $22.50, 04-516000-27

Galvanic and Pitting Corrosion—Field and Laboratory Studies, STP 576 (1976), $29.75, 04-576000-27

Stress Corrosion—New Approaches, STP 610 (1976), $43.00, 04-610000-27

Structure, Constitution, and General Characteristics of Wrought Ferritic Stainless Steels, STP 619 (1977), $7.50, 04-619000-02

A Note of Appreciation to Reviewers

This publication is made possible by the authors and, also, the unheralded efforts of the reviewers. This body of technical experts whose dedication, sacrifice of time and effort, and collective wisdom in reviewing the papers must be acknowledged. The quality level of ASTM publications is a direct function of their respected opinions. On behalf of ASTM we acknowledge with appreciation their contribution.

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Contents

Introduction

In June 1949, ASTM Committee A-10 (now Committee A-1 on Steel, Stainless Steel and Related Alloys) sponsored a *Symposium on Evaluation Tests for Stainless Steels* (*ASTM STP 93*). At that time, only one test, the boiling 65 percent nitric acid test, was an ASTM recommended practice. From the discussion at the symposium, it was clear that the nitric acid test did not always provide clear answers about whether stainless steels were susceptible to intergranular corrosion. It was also shown that other tests could be used to detect susceptibility to intergranular corrosion in stainless steels.

Building on the information presented in the 1949 symposium, considerable revision and expansion of the test methods for stainless steels were accomplished. The original ASTM Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels (A 262) were widened to include three other immersion tests: ferric sulfate-sulfuric acid, nitric acid-hydrofluoric acid, and copper-copper sulfate-sulfuric acid, besides the nitric acid. More important, perhaps, was the addition of the oxalic acid etch test which allowed for quick screening and rapid approval of acceptable material. A version of the copper sulfate-sulfuric acid without copper was introduced, withdrawn, and then reinstituted when a new need was raised.

Much of the work on the intergranular corrosion of stainless steels has been concentrated on the austenitic steels for use in the process industries. However, in the 1970s, other questions have arisen. One of the most important is whether intergranular corrosion was a necessary consideration in the high-temperature, high-purity water environment of nuclear reactors. At first thought, there could be a tendency to dismiss the problem on the grounds that the medium is too mild to be corrosive to stainless steels. Nevertheless, intergranular corrosion has been encountered in nuclear systems.

Another problem is the evaluation of ferritic stainless steels. Although the nitric acid test evolved from a simulated service test for iron-chromium alloys, testing of these steels for resistance to intergranular corrosion has been largely ignored. For example, such steels are not included in the general plan of ASTM Recommended Practice A 262 that describes what test methods are applicable to which alloys. The need for the evaluation testing of ferritic stainless steels comes from the fact that this class of

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alloys is being increasingly used in severe environments because of their resistance to chloride stress corrosion cracking. A number of ferritic stainless steels have been developed which resist intergranular corrosion in the as-welded condition, but no standard method for assessing their performance has been agreed upon.

With this background, Committees A-1 (which had absorbed A-10) and G-1 on Corrosion of Metals organized a symposium on Intergranular Corrosion of Stainless Alloys in May 1977. Three themes dominated the discussion: the state of the art in testing austenitic stainless steels, intergranular corrosion testing of stainless steels for nuclear systems, and evaluation tests for ferritic stainless steels. This volume contains the papers from that conference.

Particular attention is called to the keynote paper by M. A. Streicher which suggests a unified testing system for all stainless alloys.

R. F. Steigerwald

Climax Molybdenum Co., Ann Arbor, Mich.;
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Michael A. Streicher[1]

Theory and Application of Evaluation Tests for Detecting Susceptibility to Intergranular Attack in Stainless Steels and Related Alloys—Problems and Opportunities

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REFERENCE: Streicher, Michael A., "**Theory and Application of Evaluation Tests for Detecting Susceptibility to Integranular Attack in Stainless Steels and Related Alloys—Problems and Opportunities,**" *Intergranular Corrosion of Stainless Alloys, ASTM STP 656,* R. F. Steigerwald, Ed., American Society for Testing and Materials, 1978, pp. 3-84.

ABSTRACT: The first evaluation methods for stainless steels, the 65 percent nitric acid and the copper sulfate-sulfuric acid tests, were originally simulated service tests. Later, when the results obtained with these tests were used to prevent failures by intergranular attack in other media, they were transformed into methods of general applicability for detecting susceptibility to intergranular attack. Since the 1949 ASTM symposium on this subject, several new methods have been introduced to accomplish this goal more rapidly and effectively. This has led to a large variety of ASTM test methods which also include the nickel-rich, chromium-bearing alloys.

In an overview of all current ASTM test practices for detecting susceptibility to intergranular attack, opportunities for improvements and simplifications are discussed. New data are presented on the properties of the various copper sulfate-sulfuric acid tests and on the performance of the new iron-chromium-molybdenum ferritic stainless steels in evaluation test solutions. The need for assessment criteria for determining the occurrence of intergranular attack in all test practices is emphasized with proposals for such criteria. A plan for a greatly reduced number of improved tests is proposed. The introduction of new melting, refining, and casting methods and of new iron-chromium-molybdenum stainless steels has increased the importance of evaluation test methods and the need for improvements in ASTM test practices.

KEY WORDS: stainless steels, intergranular corrosion, ferritic stainless steels, austenitic stainless steels, nickel alloys, nitric acid, oxalic acid, etching, copper sulfates, stress corrosion, pitting, corrosion, evaluation, condensers, heat treatments, sigma phase, chromium carbides, nitrides

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[1] E. I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Del. 19898.

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Origin of Evaluation Tests

The first laboratory tests for detecting susceptibility to intergranular attack were simulated service tests. In 1926, W. H. Hatfield [*1*][2] observed intergranular attack on an austenitic stainless steel in a sulfuric acid pickling tank containing copper sulfate. To prevent the selection of material which might be susceptible to intergranular corrosion for this service, he used an 8 percent sulfuric acid solution containing copper sulfate to evaluate steels before use. By 1930, Hatfield's test solution was being used to investigate intergranular corrosion and to develop methods for overcoming this problem. B. Strauss, H. Schottky, and J. Hinnüber [*2*] and R. H. Aborn and E. C. Bain [*3*] established that the cause of intergranular attack is the precipitation of chromium carbides, $(Cr,Fe)_{23}C_6$) at grain boundaries. Because these chromium-rich precipitates are surrounded by metal which is depleted in chromium, there is more rapid attack at these zones than on undepleted metal surfaces. To prevent precipitation of chromium carbides, titanium and niobium were added. These elements combined with carbon, which was present in relatively large concentrations (up to 0.15 percent) in the alloys made at that time.

In 1930, W. R. Huey [*4*] described another simulated service test used at the du Pont Company since 1927 to detect variations in the performance of iron-12 to 18 percent chromium alloys intended for service in nitric acid plants. For rapid results, he selected a concentrated solution of 65 percent nitric acid, which is near the constant boiling concentration of 68.5 percent. Five 48-h periods, each with fresh acid solution, were proposed. The weight loss was converted to a corrosion rate. A glass flask fitted with a reflux condenser via a ground glass joint was specified. Later, the less costly cold finger condenser was used at many laboratories, apparently without recognition that this change in condensers can affect corrosion rates.

It was soon found that among the variables were certain heat treatments which made not only the ferritic stainless steels subject to intergranular attack, but also the austenitic, 18Cr-8Ni alloys. From this simulated service test in boiling 65 percent nitric acid, there evolved ASTM Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels (A 262). Its large-scale use by one of the first and largest purchasers of stainless steels made it the leading method for acceptance testing of stainless steels in the United States.

In England and Germany, the copper sulfate test with sulfuric acid has been the most frequently used. Evaluation in this 72-h test is by examination for fissures (cracks) on the test specimen, which is bent after exposure to the test solution. In the United States, this test was not stan-

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

dardized by ASTM until after 1949. ASTM A 393 specified a solution of 6 percent anhydrous copper sulfate and 16 percent sulfuric acid (by weight).

Differences in the results derived from these two test methods and the problems of correlating laboratory test results with service performance necessitated an extensive comparison of stainless steels in the two tests. The introduction of extra low-carbon (ELC) grades and the discovery of intermetallic phases in austenitic stainless steels contributed to these problems. In preparation for the ASTM "Symposium on Evaluation Tests for Stainless Steels" [5] held in June 1949, nine laboratories carried out numerous tests to increase the reproducibility of the test methods, to determine optimum sensitizing treatments to be applied to alloys (ELC and titanium or niobium stabilized) which were to be welded, and to define the sigma-phase phenomenon. Sigma-phase is an intermetallic compound. However, it was later found that the presence of submicroscopic phases or equilibrium segregation of molybdenum at the grain boundaries or both could also lead to rapid intergranular attack.

Some of the participants in the symposium used a third acid solution in their test programs, a solution containing 3 percent hydrofluoric and 10 percent nitric acid at 70°C. According to D. Warren [6], this solution was being used in 1929 by several laboratories to descale stainless steels which had been given sensitizing heat treatments. In some cases, the specimens completely dissolved because of rapid intergranular attack. This led to the use of the nitric-hydrofluoric acid solution for revealing the presence of weld-decay zones on weldments.

Probably the most important findings of the 1949 symposium were:

1. In austenitic stainless steels containing molybdenum, sigma-phase may be formed at grain boundaries, and its presence is detected only by the nitric acid test and not by the acid copper sulfate or nitric-hydrofluoric acid tests.
2. The 72-h acid copper sulfate test period is much too short to detect susceptibility to intergranular attack. As long as 600 h are needed in this test to reveal the kind of susceptibility detected in only 240 h by the nitric acid test.

The finding that certain stainless steels may contain sigma-phase, which makes them susceptible to intergranular attack only in nitric acid, accounted for most of the discrepancies between the various test methods. However, there were also other causes for discrepancies, such as a lack of standardized testing conditions and apparatus and unrecognized factors in the corrosion of stabilized alloys, Types 321 and 347 (analyses in Table 1). These problems and the absence of extensive correlations between service performance and laboratory test results led some to challenge the applicability of the laboratory tests. A commonly held conviction was expressed by H. W. Gillette [7] at the symposium. In his review, "Present Knowledge of Low-Carbon 18-8," he concluded that "artificial, conventional

TABLE 1—*Nominal compositions of stainless steels and related alloys.*[a]

	Composition, percent by weight				
Type	Chromium	Nickel	Molybdenum	Carbon, max	Other
430	14.0 to 18.0	. . .	. . .	0.12	Mn—1.0 max; Si—1.0 max
446	23.0 to 27.0	. . .	. . .	0.20	Mn—1.50 max; Si—1.0 max; N—0.25 max
304	18.0 to 20.0	8.0 to 12.0	. . .	0.08	Mn—2.0 max; Si—1.0 max
304L	18.0 to 20.0	8.0 to 12.0	. . .	0.03	Mn—2.0 max; Si—1.0 max
310	24.0 to 26.0	19.0 to 22.0	. . .	0.25	Si—1.50 max
316	16.0 to 18.0	10.0 to 14.0	2.00 to 3.00	0.08	Mn—2.0 max; Si—1.0 max
316L	16.0 to 18.0	10.0 to 14.0	2.00 to 3.00	0.03	Mn—2.0 max; Si—1.0 max
317L	18.0 to 20.0	11.0 to 15.0	3.0 to 4.0	0.03	Mn—2.0 max; Si—1.0 max
321	17.0 to 19.0	9.0 to 12.0	. . .	0.08	%Ti = 5 × %C min
347	17.0 to 19.0	9.0 to 13.0	. . .	0.08	Cb = 10 × %C min
Carpenter 20 Cb-3	19.0 to 21.0	32.5 to 35.0	2.00 to 3.00	0.06	%Cb + Ta = 8 × %C; Cu—3.00 to 4.00
Hastelloy Alloy C	14.5 to 16.5	~54	15.0 to 17.0	0.08	Fe—5.5; W—4; Co—2.5
Hastelloy Alloy C-276	14.5 to 16.5	~54	15.0 to 17.0	0.02	W—4; Co—2.5 max; Si—0.05 max
Hastelloy Alloy G	18.0 to 21.0	~50	5.5 to 7.5	0.05	Cu—2; Nb—2; Fe—19.5
Inconel Alloy 600	14.0 to 17.0	72 min	. . .	0.15	Fe—8; Cu—0.5
Inconel Alloy 625	20.0 to 23.0	~62	8.0 to 10.0	0.10	Cb—3.6; Fe—5 max
Incoloy Alloy 800	19.0 to 23.0	30.0 to 35.0	. . .	0.10	Ti—0.5; Cu—0.75; Fe ~45
Incoloy Alloy 825	19.5 to 23.5	38.0 to 46.0	2.5 to 3.5	0.05	Ti—0.9; Cu—2.2; Fe—33

[a] Compositions for other ferritic stainless steels are given in Tables 6 and 7.

methods for evaluating sensitization and corrosion resistance are incompetent to appraise truly the material for a given actual service. Specifications calling for such tests may discard perfectly satisfactory material."

To resolve questions raised at the symposium, F. L. LaQue [*8*] concluded his extensive summary and discussion of the papers presented with a list of "Indicated Activities" to be initiated. These included the following items:

1. Standardize the acid copper sulfate test and the nitric-hydrofluoric acid test.
2. Catalogue corrosive environments with respect to whether the boiling nitric acid or the acid copper sulfate test of sensitized alloys gives the more significant results or whether neither gives significant results.
3. Undertake extensive field tests of welded and sensitized specimens in a variety of media for long periods and correlate with results of evaluation tests.
4. Determine environments in which sigma-phase is likely to be harmful.
5. Establish heat treatments more closely representative of the sensitizing effects of normal welding operations.

Of these items, only the last has not yet been accomplished. Attempts to define a simple, synthetic heat treatment which closely simulates the thermal cycles encountered during welding have not been successful. Such a heat treatment would be applied before evaluation testing to specimens representing material to be welded during fabrication. The results would then show whether or not welding of this material during fabrication would make the weldments susceptible to intergranular attack. Nor has it been possible to standardize the measurement of corrosion of the various components of a weldment, that is, weld metal, fusion zone, heat-affected zone and base plate, after exposure to an evaluation test solution. These problems are discussed later in this paper.

In numerous additional laboratory tests, it was established that sigma-phase in molybdenum-bearing austenitic stainless steels (Types 316, 316L, 317, and 317L) makes these alloys subject to intergranular attack only in nitric acid [*6,9*]. To establish whether this conclusion also applies to plant solutions, extensive field tests were undertaken with welded and sensitized specimens in a variety of media for long periods, and the results were correlated with laboratory evaluation tests. J. R. Auld [*10*] reported on an extensive test program carried out in various plants of the du Pont Company. Another extensive plant test program was sponsored by the Welding Research Council (WRC). The results were summarized in WRC Bulletin No. 138, February 1969. They confirmed that sigma-phase in the just-mentioned alloys is a problem only in nitric acid environments.

Comprehensive reviews of research on intergranular corrosion of stainless steels and nickel-rich alloys have been recently published by M. Henthorne [*11*] and by R. L. Cowan and C. S. Tedmon [*12*]. In these reviews, the formation of precipitates at grain boundaries and mechanisms of intergranular attack have been emphasized. The present article consists of a discussion, based in part on new data, of the characteristics of evaluation test methods, the background of several new evaluation tests, and of opportunities for improvements of standard test methods, together with a new list of "Indicated Activities."

In the previous discussion and also in the rest of this paper, the frequently used terms "Strauss test" and "Huey test" have been avoided. As described earlier, the test in sulfuric acid with copper sulfate was originated by W. H. Hatfield rather than by B. Strauss. Also, there are at least three different versions of this test solution currently in use, none of which is like that used by Hatfield. There may also be confusion when the name of an originator who has introduced more than one test is applied to a test method. For these reasons, and because so many different tests are discussed, more precise and informative terms are used for the test methods throughout this paper.

Developments Since the Symposium of 1949

Because all of the early evaluation test solutions were derived from simulated service tests, there was considerable resistance to the application of test results for the many entirely different service environments. Why test in boiling 65 percent nitric acid if the steel is not to be used in a nitric acid environment? M. H. Brown, W. B. DeLong, and W. R. Myers [*13*] emphasized in the 1949 symposium that "the primary purpose of the boiling 65 percent nitric acid test is to detect the susceptibility of stainless steels to intergranular corrosion. In this sense, and *only* in this sense, the results are applicable to any media capable of attacking susceptible material intergranularly." However, as already mentioned, it was found that the nitric acid test detects susceptibility to intergranular attack associated not only with chromium carbides, but also with sigma-phase in molybdenum-bearing alloys. In addition, W. B. DeLong [*14*] showed that chromium as a corrosion product increases the rate of corrosion by nitric acid. J. E. Truman [*15*] demonstrated that divalent chromium is converted to the tri- and then the hexavalent states. Furthermore, it was shown [*16*] that hexavalent chromium not only causes a rapid increase in the rate of intergranular attack on sensitized material, but also causes intergranular attack on solution-annealed material, that is, on grain boundaries which are free of chromium-carbide and sigma-phase precipitates.

The concentration of hexavalent chromium increases most rapidly at susceptible grain boundaries and in pits formed when nonmetallic inclusions, including titanium carbides, are dissolved by nitric acid. As a result, there is more rapid intergranular attack extending from these pits into the metal than elsewhere on the surface from which corrosion products enter the test solution and become diluted in it. This form of preferential attack is particularly marked on cross sections of bar stock and tubes on which the cross sections of elongated inclusions are exposed to the test solution. In this form, preferential attack by hexavalent chromium is known as end grain corrosion. Because sigma-phase in molybdenum-bearing steels and hexavalent chromium effects are unique to nitric acid environments, objections to the use of the nitric acid test for evaluating some materials which will not be exposed to nitric acid are justified.

Another frequently voiced objection was the length of testing time, ten days, required for the nitric acid test. When this period is added to the time required for shipment of the material to be tested from the supplier to the user's laboratory, preparation of the test specimen, including, in some cases, heat treatments, the total time elapsed between shipment of the test material and calculation of corrosion rates becomes a minimum of two to three weeks. These problems led first to the development of a rapid metallographic method for screening acceptable material from the nitric acid test and then to a shorter boiling acid test which was designed to detect only that susceptibility to intergranular attack which is associated with chromium carbide (and nitride) precipitates.

Oxalic Acid Etch Test

The purpose of the two new tests was to provide rapid standard methods for detection of the presence and extent of chromium depletion associated with chromium carbide and nitride precipitates. Thus, they were merely to be a means for detecting structural changes in stainless steels which were known to reduce appreciably the resistance of these alloys to intergranular attack in acids and to some other forms of corrosion. No attempt was made to simulate such service environments. In the oxalic acid etch test [*17,18*], a polished specimen of austenitic stainless steel is etched electrolytically in a 10 percent solution of oxalic acid at room temperature. The specimen is polarized anodically by a relatively large current for a standardized time period, 1 A/cm^2 for 1.5 min. These drastic etching conditions were selected to overetch the surface and thereby facilitate classification of microscopic etch structure by nonspecialists. In the absence of chromium carbide precipitates, differences in the rate of etching of variously oriented grains result in steps at the grain boundaries (Fig. 1). When the steel contains chromium carbide precipitates at grain boundaries, their effect depends on their concentration and distribution. The standard etching conditions produce deep grooves or ditches at the boundaries, which may or may not completely surround the grains (Figs. 2,3). To standardize the test, the etch structures were classified into three categories: (*a*) *step,* steps between the grains, no ditches at grain boundaries, (*b*) *dual,* some ditches at grain boundaries, but no single grain completely surrounded

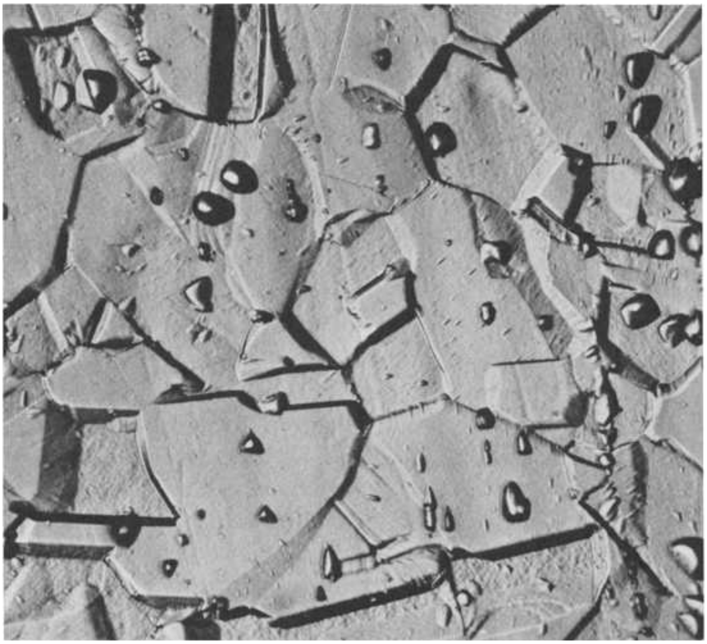


FIG. 1—*Oxalic acid etch* [17,18] (×*500*). *Step structure. Etched 1A/cm^2 for 1.5 min.*

by ditches, and (*c*) *ditch,* one or more grains completely surrounded by ditches (Figs. 1 to 3).

These structures are used to screen wrought and cast austenitic stainless steel specimens from testing in the various acid corrosion tests. For example, all Types 304 and 304L specimens having a step or dual structure are known to have low corrosion rates because they are essentially free of intergranular attack. Therefore, there is no need to test them further in tests which require between 72 and 240 h. Because the rates of corrosion in the acid corrosion tests of specimens containing grains which are completely surrounded by ditches (ditch structure) may range from low to very high depending on the severity of chromium carbide precipitate, they must be evaluated in the hot acid corrosion tests.

Examples of slight and severe sensitization are shown in Fig. 4. The corrosion rate (slope of the weight-loss-time line) of the carbide-free, solution-annealed specimen (step structure) is low and constant with time in the nitric acid test. Heating the 0.06C Type 304 specimen for 1 h at 677°C (1250°F) severely sensitizes it (ditch structure), and its rate (slope) increases rapidly with time after 100 h of testing. The 0.022C alloy also has a ditch structure after heating 1 h at 677°C but only a relatively small amount of carbide precipitation. Its corrosion rate after 240 h, the standard

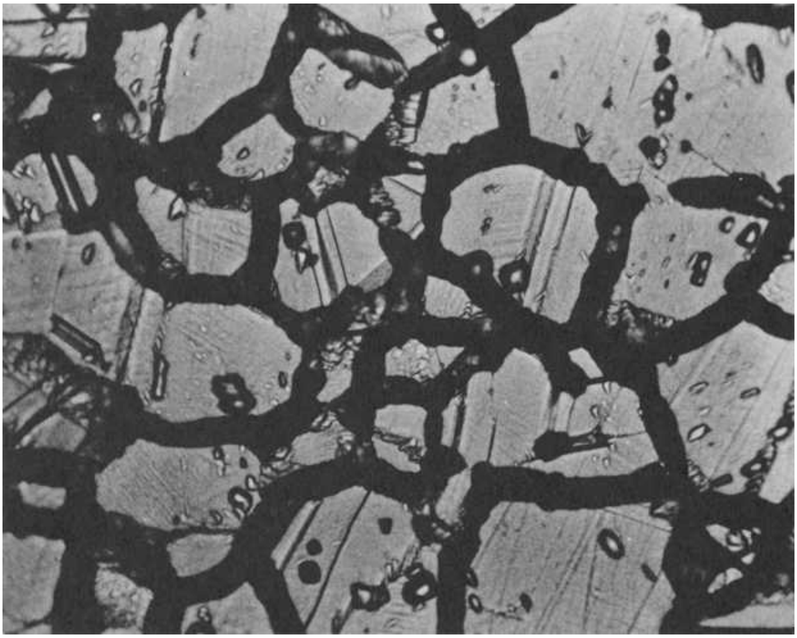


FIG. 2—*Oxalic acid etch* [17,18] *(×500). Ditch structure. Etched 1 A/cm*^{2} *for 1.5 min.*

testing time, is as low as that of the solution-annealed material. Only after more than 240 h is there a gradual increase in corrosion rate caused by the slight degree of sensitization. Both Specimens B and C have acceptable corrosion rates.

Ferric Sulfate-Sulfuric Acid Test

The boiling ferric sulfate-50 percent sulfuric acid test was derived from a study [*19*] of acid corrosion of stainless steels and its inhibition by ferric salts. It was found that ferric salts effectively inhibit corrosion of stainless steels but do not prevent intergranular attack on sensitized steels, that is, specimens containing chromium-depleted zones surrounding chromium carbide precipitates at grain boundaries. In 10 percent sulfuric acid containing ferric sulfate inhibitor, there is a gradual increase in corrosion rate (slope of curve) of the sensitized specimen with time after 200 h of immersion in boiling solution (Fig. 5). The rate increases with time because grains are undermined and dislodged. To increase the rate of intergranular attack, concentrations of sulfuric acid ranging up to 60 percent where explored (Fig. 6). Between 50 and 60 percent acid, there is a large increase in weight loss at a given exposure time, for example, after 50 h.

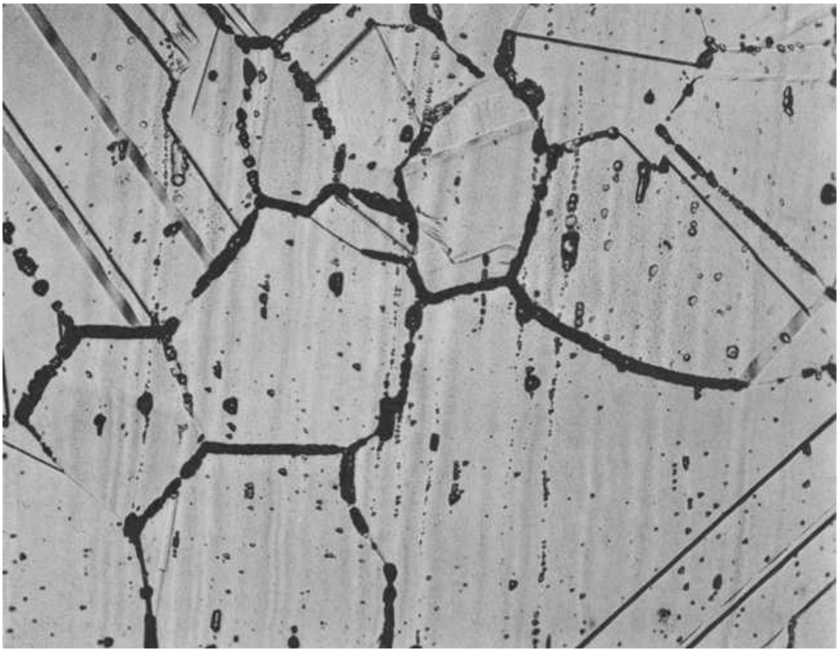


FIG. 3—*Oxalic acid etch* [17,18] *(×250). Dual structure. Etched 1A/cm² for 1.5 min.*

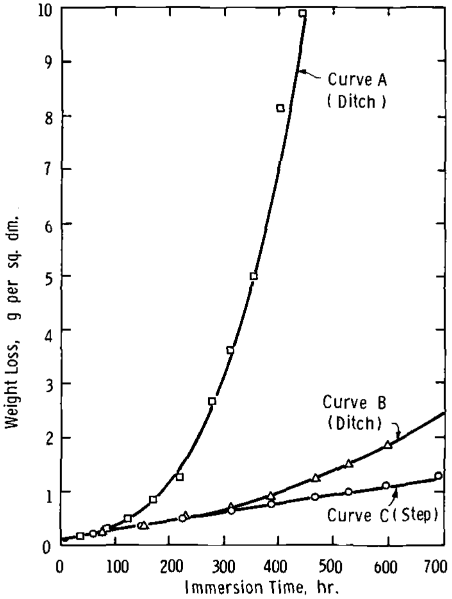
This is a result of the increase in acid concentration and the concurrent increase in boiling temperature. The optimum concentration for evaluation testing is a compromise between a sufficient degree of control to assure adequate reproducibility and the need for as short a testing time as possible. For austenitic stainless steels, a solution with 50 percent sulfuric acid and a testing time of 120 h were selected [*16,20*].

The ferric sulfate in sulfuric acid solutions makes stainless steels passive. Both the grain faces and the grain boundaries, even on sensitized specimens, have a corrosion potential of +0.6 V versus saturated calomel electrode (SCE). There is no hydrogen evolution because the cathodic reaction consists of the reduction of ferric to ferrous ions

$$\mathrm{Fe}^{+3} \xrightarrow{+e} \mathrm{Fe}^{+2}$$

Ferric ions are consumed in amounts which are electrochemically equivalent to the stainless steel dissolved

$$\left.\begin{matrix}\mathrm{Fe}\\ \mathrm{Cr}\\ \mathrm{Ni}\end{matrix}\right\} \xrightarrow{-e} \mathrm{Fe}^{+2},\mathrm{Cr}^{+2},\mathrm{Ni}^{+2}$$



(*a*) 0.06 percent carbon, heated 1 h at 677 °C.
(*b*) 0.022 percent carbon, heated 1 h at 677 °C.
(*c*) Solution-annealed condition.

FIG. 4—*Corrosion of Types 304 and 304L stainless steels in boiling 65 percent nitric acid test* [17].

In the passive state, an adherent protective film is formed on the metal surface. Its nonuniform dissolution controls the rate of corrosion. There is continuous dissolution and repair of the passive film at discrete points in the surface [*16,19*]. On chromium-depleted surfaces surrounding chro-

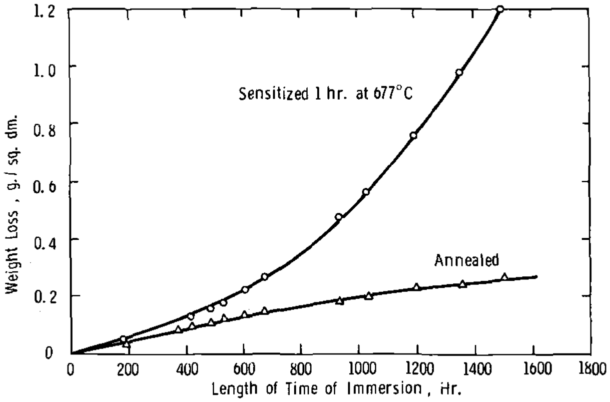


FIG. 5—*Corrosion of Type 304 steel in inhibited boiling 10 percent sulfuric acid. Inhibitor 0.47 g Fe*$^{+3}$*/litre, added as ferric sulfate.*

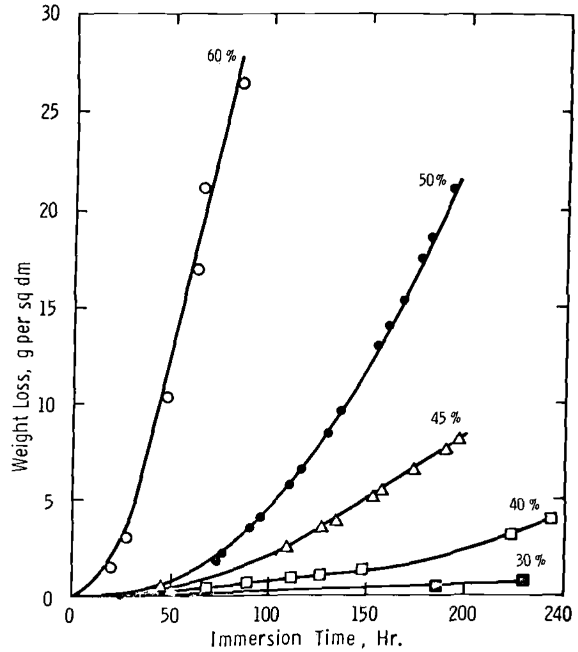


FIG. 6—*Effect of concentration of sulfuric acid on corrosion of sensitized Type 304 stainless steel in boiling ferric sulfate-sulfuric acid solution* [16,20]. *Specimen: 0.06 percent carbon, heated 1 h at 677°C. Solutions: the boiling temperature increases from 102°C for 10 percent acid to 140°C for 60 percent acid (weight percent).*

mium carbide precipitates, the protective film is more soluble in the acid, and therefore, more metal must dissolve to repair the film. Thus, the boundaries are not active. There is no hydrogen evolution. In boiling 50 percent sulfuric acid, any active site would immediately activate the entire specimen. This is demonstrated by the galvanic action produced by oxide scale inadvertently left on the surface of the specimen or by contact of the specimen with an iron rod. In both cases, there is immediate conversion of the entire specimen to the active state with almost explosive evolution of large amounts of hydrogen gas.

Corrosion products do not affect the corrosion rates in the ferric sulfate-sulfuric acid test. Thus, the ratio of surface area of specimens to the solution volume is not critical and solution changes are not necessary during the 120-h test period. The only precaution necessary is to maintain enough ferric ions in the solution to maintain the passive state. For every gram of stainless steel dissolved, about 10 g of $Fe_2(SO_4)_3 \cdot X\ H_2O$ are needed.

The ferric sulfate-sulfuric acid test does not detect sigma-phase in Types 316, 316L, 317, and 317L stainless steels. Therefore, the oxalic acid etch test can be used to screen not only Types 304 and 304L steels, but also the previously mentioned molybdenum-bearing grades. This is shown in Table 2 by data on Types 304, 316, and 316L steels. For a given alloy, the ratios of the corrosion rate of a sensitized specimen to that of an annealed specimen are given for both the ferric sulfate and the nitric acid tests. The use of ratios, by eliminating the effect of alloying elements on general corrosion, provides a measure of the sensitivity of a test for detecting susceptibility to intergranular attack in a given test period. On the two Type 304 stainless steel heats, the ratios in the 120-h ferric sulfate test are essentially the same as those obtained in the 240-h nitric acid test. Thus, in the ferric sulfate test, a certain degree of susceptibility to intergranular attack associated with chromium carbide precipitates can be detected in one half the time required in the nitric acid test.

The two Type 316L steels of Table 2 were selected because they do not show any carbide precipitate after heating 1 h at 677 or 704°C (1250 or 1300°F). They have a step structure in the oxalic acid etch. Nevertheless, in the nitric acid test, intergranular attack is so severe that the sensitized specimens have corrosion rates 133.0 and 35.6 times greater than the corresponding annealed specimens. The ratios of 1.0 and 1.4 in the ferric sulfate test show that in this solution the rates of these "sensitized" Type 316L steels are the same as those of the annealed counterparts. The submicroscopic or invisible precursor to sigma-phase results in intergranular attack only in the nitric acid test. It is apparent why the oxalic acid etch test cannot be used to screen Type 316L stainless steels for the nitric acid test. The ratios and oxalic acid etch structure for the Type 316 steel in Table 2 show that sensitization in this alloy with 0.046 percent carbon is a result of the presence of both chromium carbide and submicroscopic sigma-phase or equilibrium segregation.

The nitric hydrofluoric and the various copper sulfate-sulfuric acid tests

TABLE 2—*Effect of chromium carbide and "sigma-phase" on intergranular corrosion* [16].

Alloy		Ratios of Corrosion Rates[a]		Oxalic Acid Etch Structure, (sensitized specimen)
AISI	%C	Ferric Sulfate-50% Sulfuric Acid, 120 h	65% Nitric Acid, 240 h	
304	0.063	11.8	12.8	Ditch
304	0.031	2.1	2.0	Ditch
316L	0.022[b]	1.0	133.0	Step
316L	0.020	1.4	35.6	Step
316	0.046	7.8	19.0	Ditch

[a] $\dfrac{\text{Rate of sensitized specimen}}{\text{Rate of solution annealed specimen}}$. Sensitizing heat treatment 1 h at 677°C (1250°F).

[b] Sensitized 1 h at 704°C (1300°F).

also detect only susceptibility to intergranular attack associated with chromium carbide precipitate and do not detect that associated with submicroscopic sigma-phase [*9,13,16,21*].

Nitric-Hydrofluoric Acid Test

Because this solution detects only the chromium carbide type of susceptibility to intergranular attack, it too is suitable for evaluating those molybdenum-bearing stainless steels which are not intended for service in nitric acid. Corrosion in this solution is very sensitive to variations in chromium content within the nominal ranges, for example, 16 to 18 percent chromium in Type 316. Therefore, it is not possible to specify for a given type of stainless steel a corrosion rate which separates material resistant to intergranular attack from material which is susceptible to attack. To eliminate the effect of variations in alloy content, the ratio of rates, such as is shown in Table 2, was introduced [*16*]. For this purpose, two specimens of the same heat must be tested, the "unknown" and a solution-annealed specimen which is known to be free of susceptibility to intergranular attack. D. Warren [*22*] applied one of the previously used [*23*] testing conditions, 3 percent hydrofluoric acid-10 percent nitric acid solution at 70°C, to 80 heats of Types 316 and 316L steels. On the basis of this study, he proposed two 2-h test periods and a ratio of 1.5 to separate susceptible from nonsusceptible materials.

Because of the hydrofluoric acid in this test solution, glass equipment cannot be used. Cylinders and specimen holders must be made from polyvinyl chloride, and great care must be exercised to prevent loss of hydrofluoride vapor from the test solution, both during the heat up and the test period. Because the 70°C test temperature is below the boiling point, the plastic vessels must be heated in a carefully controlled water bath.

Copper Sulfate-16 Percent Sulfuric Acid Test

In 1955, the copper sulfate-sulfuric acid test with approximately 6 percent copper sulfate and 16 percent sulfuric acid[3] became ASTM Recommended Practice A 393. A test period of only 72 h was recommended, even though it had been already concluded at the 1949 symposium "that acidified copper sulfate tests must be continued for at least several hundred hours before it can be assumed that intergranular corrosion would not occur" [*13*]. In Germany, the rate of intergranular attack in this solution has been greatly increased by H. J. Rocha [*24,25*] since 1950. He added zinc dust to precipitate metallic copper [*24*] and later embedded the stain-

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[3] Actual concentrations specified were 5.7 percent copper sulfate and 15.7 percent sulfuric acid.

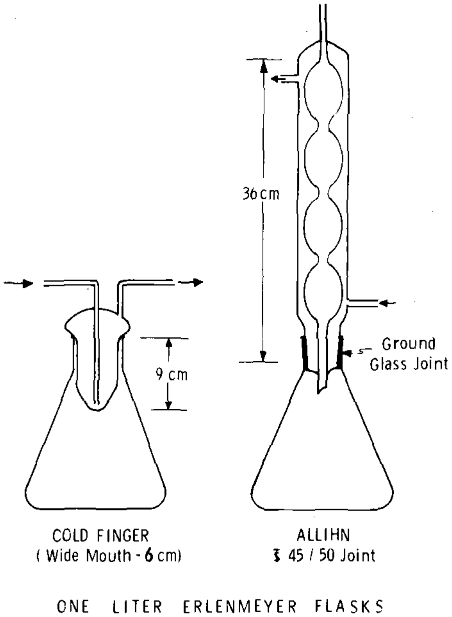

FIG. 7—*Types of condensers.*

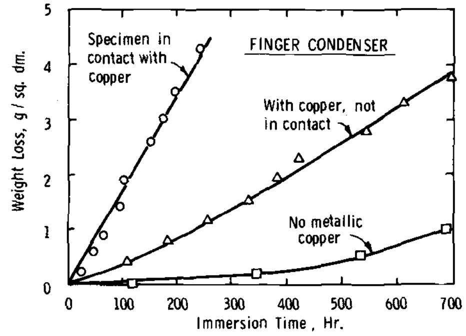

FIG. 8—*Corrosion of sensitized Type 316 steel in boiling copper sulfate-sulfuric acid solution* [16]. *Specimen: 17.4Cr; 12.7Ni; 1.89Mo; 0.053C. Heated 1 h at 677°C (EW-6). Solution: 15.7 percent sulfuric acid with 5.7 percent anhydrous copper sulfate.*

less steel specimens in metallic copper chips or shot. This has the effect of changing the corrosion potential of the test specimen in the less noble direction to that of the metallic copper and thereby reducing the testing time from 200 to less than 48 h.

Quantitative measurements of the effect of metallic copper in the copper sulfate-sulfuric acid solution on intergranular attack were reported by

M. A. Streicher [*16*] in 1959. Three types of tests were made in flasks with cold finger or pine cone condensers (Fig. 7) (a) without metallic copper, (*b*) with a specimen of copper not in contact with the stainless steel specimen, and (*c*) with copper (turnings) in contact with the stainless steel specimen. Results are shown in Fig. 8. Simultaneous immersion of a copper specimen increased the rate of corrosion on a sensitized Type 316 specimen by a factor of 8 in a 200-h test period. Contact of the stainless steel with the copper increased this factor to 34. L. R. Scharfstein and C. M. Eisenbrown [*26*] confirmed these effects of simultaneous immersion of copper and contact with copper on sensitized stainless steel specimens which they bent after testing and examined for fissures. They also used flasks with finger condensers.

The three electrode potentials plotted in Fig. 9 provide data on the changes taking place in the cupric sulfate-sulfuric acid solutions during these tests in a flask with a finger condenser. As in the case of ferric ions, cupric ions make stainless steels passive in sulfuric acid. Measurements on the platinized platinum electrode give the oxidation-reduction potential of the solution. The potentials on the stainless steel and the copper specimens are the corrosion potentials of these materials. In the presence of the stainless steel specimen whose corrosion potential is constant, there is a gradual decrease (change in the active direction) in the redox potential of the solution resulting from the formation of cuprous ions on the surface of the specimen

$$\mathrm{Cu}^{+2} \xrightarrow{+e} \mathrm{Cu}^{+1} \tag{1}$$

This produces a change in the relative concentrations of cupric and cuprous ions. The rate of this change is greatly increased by the addition

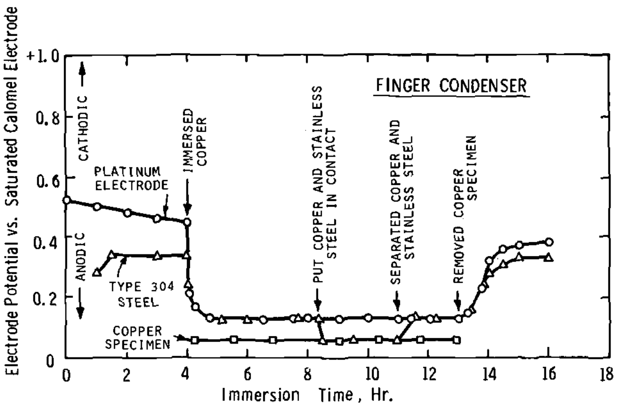

FIG. 9—*Electrode potential measurements in boiling copper sulfate-sulfuric acid solution* [16]. *Solution: 15.7 percent sulfuric acid with 5.7 percent anhydrous copper sulfate.*

of metallic copper (40 cm^2 surface area in 600 ml) whose dissolution is governed by the rate of the cathodic reaction

$$Cu + Cu^{+2} \rightarrow 2\,Cu^{+1} \qquad (2)$$

Within an hour, the potentials of the stainless steel and of the platinized platinum electrode become constant at +0.13 V versus SCE, that is, the stainless steel assumes the redox potential which remains constant at a relatively low potential. However, the corrosion potential of the copper specimen is even lower, and, when contact is made between the stainless steel specimen and the copper, the steel assumes the potential of the copper. The redox potential (platinum electrode) remains unchanged. Reversing these steps, that is, breaking contact and removing the metallic copper, reverses the potential changes. The potentials of the platinized platinum and the stainless steel move in the noble direction.

In later tests with *Allihn*-type condensers (Fig. 7), W. Schwenk et al [*27,28*] did not observe differences between the corrosion potentials of stainless steel and copper. We have confirmed this finding and also found, as might be expected in the absence of this difference in potentials, that there is little, if any, difference in corrosion rates between tests made with or without contact between the copper and stainless steel. This is shown in Fig. 10 for the same heat of sensitized Type 316 steel as was used for the tests of Fig. 8.

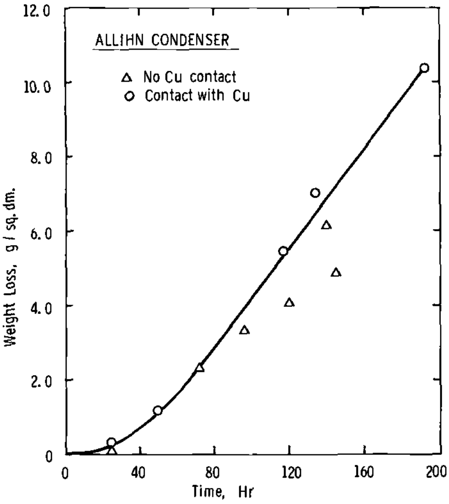

FIG. 10—*Effect of copper on corrosion of sensitized Type 316 steel in copper sulfate-sulfuric acid solution. Specimen: EW-6, 0.053 percent carbon, heated 1 h at 677°C. Solution: 15.7 percent sulfuric acid with 5.7 percent anhydrous copper sulfate.*

To obtain additional quantitative data on the effect of the condenser on intergranular attack, tests were made about ten years ago, but not previously published, with the two types of condensers with simultaneous immersion of copper, but not in contact with the stainless steel specimens. Weight loss was measured on both the stainless steel and the copper. Two specimens (10 cm^2) of sensitized Type 316 stainless steel (17.4 percent chromium, 12.7 percent nickel, 1.89 percent molybdenum, 0.053 percent carbon, 0.44 percent silicon, 1.60 percent manganese) were tested in identical (600-ml) copper sulfate-sulfuric acid solutions with the copper specimens having an area of about 20 cm^2. One was started in a flask with an Allihn[4] condenser and the other with a wide-mouth Erlenmeyer flask fitted with a cold finger condenser (Fig. 7). After 120 h, the stainless steel and copper specimens were switched. The specimens which had been in the flask with the Allihn condenser were placed in the flask with the finger condenser and vice versa.

Whether started in the Allihn condenser test or switched into it, the rate of intergranular attack on sensitized stainless steel is much higher with this condenser than with the finger condenser (Fig. 11). In contrast, weight loss measurements on the copper specimen (Fig. 12) give the reverse picture. The test with the finger condenser always has a much higher rate than that in the flask with the Allihn condenser. On copper,

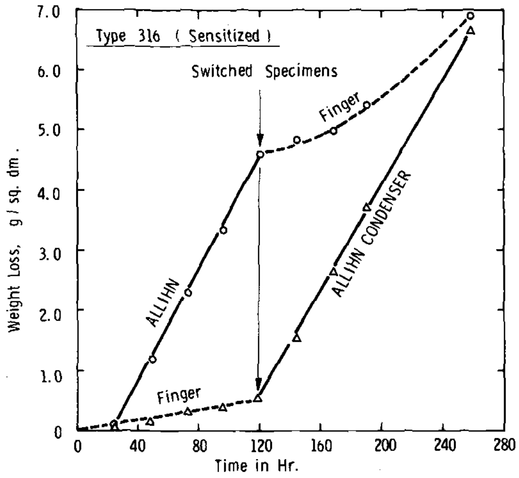

FIG. 11—*Effect of the type of condenser on corrosion of two sensitized Type 316 stainless steel specimens in boiling copper sulfate-sulfuric acid solution. Specimens: EW-6, 0.053 percent carbon, heated 1 h at 677°C, water quenched. Solution: 15.7 percent sulfuric acid with 5.7 percent anhydrous copper sulfate. With metallic copper not in contact with the stainless steel specimens.*

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[4] The Allihn condenser with a 45/60 ground glass joint is a standard laboratory item in the United States. It was originally designed for use with the SOXHLET extraction apparatus.

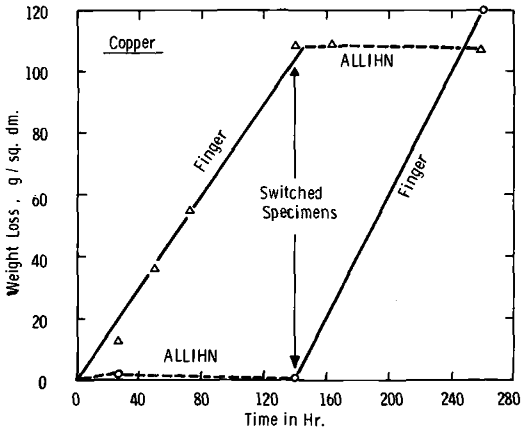

FIG. 12—*Effect of the type of condenser on corrosion of copper in boiling copper sulfate-sulfuric acid solution. Same tests as Fig. 11. Copper specimens about 15 cm² and solution volume 600 ml.*

after an initial weight loss during the first 24 h, there actually is a weight gain whenever the copper is exposed in a flask with an Allihn condenser. This is shown in greater detail by the data in Table 3. After 24 h, there is deposition of copper on the copper specimen in the flask with the Allihn condenser (Fig. 13).

Similar results were obtained on sensitized Type 304 stainless steel (Table 4). In a 183-h test without metallic copper, the weight loss of the specimen tested in the solution with the Allihn condenser was 14 times greater than that exposed in the solution with a finger condenser. In a 144-h test with metallic copper on duplicate specimens heated 2 h at

TABLE 3—*Dissolution of copper in boiling $CuSO_4$-$15H_2SO_4$. The effect of the type of condenser (71 g $CuSO_4 \cdot 5H_2O$ in 600 ml).*

	Weight Loss, g/dm²		
Time, h	Cu-34, Finger	Cu-41, Allihn	Ratio Finger/Allihn
24	13	1.3	9.6
48	35	1.2	29
72	55	1.0	55
140	108	0.2	460
Specimens switched	Allihn	Finger	
162	109	82	. . .
261	108	129	. . .

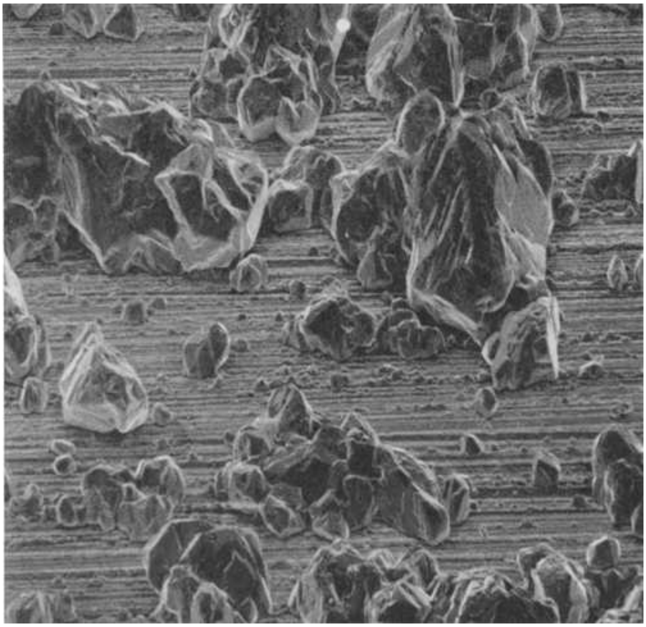

FIG. 13—*Crystallization of copper on copper* (×*200*). *Copper exposed 18.5 h in boiling 15 percent sulfuric acid with copper sulfate (Allihn condenser). Scanning electron micrograph.*

677°C, corrosion in the flask with the Allihn condenser was 17.5 times greater than that on specimens in the flask with the finger condenser, while the ratio for corrosion on the metallic copper was only 0.01.

From Figs. 11 and 12, it is apparent that copper sulfate-sulfuric acid tests should be made in flasks equipped with Allihn condensers. With this apparatus, susceptibility to intergranular attack is most rapidly revealed. Also, changes in the solution produced by dissolution of copper are minimized because the rate of dissolution of copper is very low. Finally, with this condenser, it is not essential that there be electrical contact between the stainless steel test specimen and the metallic copper. These findings

TABLE 4—*Attack on sensitized Type 304 steel in copper sulfate test.*

	Weight Loss, g/dm^2			
Type of Condenser	183 h	226 h	272 h	343 h
Finger	0.1263	0.1583	0.2160	0.2865
Allihn, short drip tip	1.7714	3.0928	8.2849	...

NOTE—Solutions: 15% H_2SO_4 + $CuSO_4$, no metallic copper. Specimens: Type 304 steel, heated 2 h at 677°C.

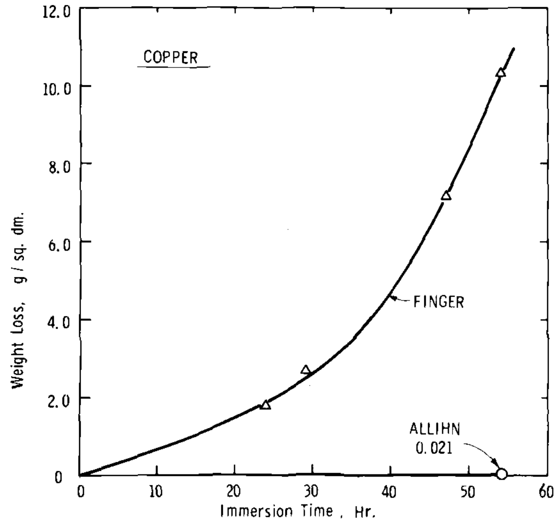

FIG. 14—*Effect of type of condenser on corrosion of copper in boiling 15 percent sulfuric acid. Solution: 600-ml acid, no copper sulfate added. No change in solution. Specimens: about 14 cm^2.*

have been incorporated into the new ASTM Practice for Ferritic Alloys and into Practice E of A 262.

The rate of dissolution of copper is a function of the concentration of oxidizing species in the acid [*29*]. To obtain data on the presence of oxidizing agents (air) as a function of the type of condenser, copper was exposed to "pure," boiling 15 percent sulfuric acid, that is, without copper sulfate or a stainless steel specimen. The results have been plotted in Fig. 14. As in the case with cupric sulfate present, the rate of corrosion is much greater in the flask with the finger than with the Allihn condenser. The increase in rate with time can be attributed to two processes involving dissolved oxygen: (*a*) the removal of hydrogen atoms from the copper specimen, that is, cathodic depolarization and (*b*) the oxidation of cuprous to cupric ions, which then increases the dissolution of copper in accordance with Eq 2.

On the basis of these results on copper, it may be concluded that the finger condenser produces a higher concentration of oxygen in the test solution than does the Allihn condenser. In contrast, on stainless steels, it can be expected that, as shown in Fig. 11, the greater concentration of oxygen promotes the passive state and thereby reduces the rate of attack with the finger condenser as compared with the Allihn condenser, which provides less oxygen.

Additional data on the effect of oxygen were obtained by purging the test solutions with air or nitrogen (Figs. 15,16). As expected, purging the

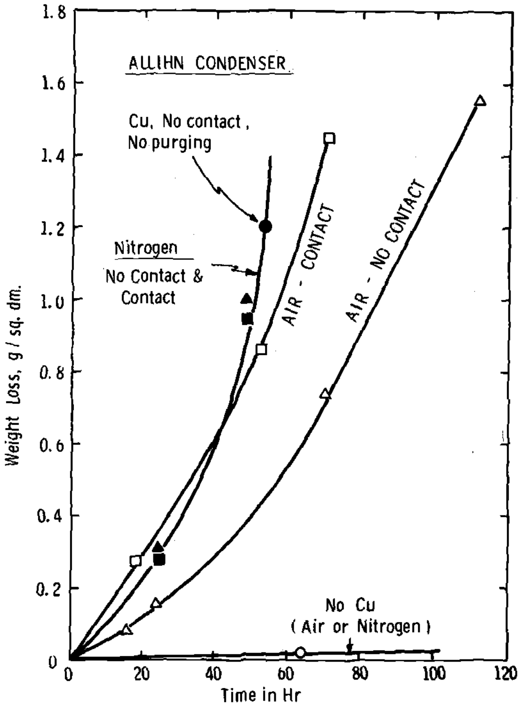

FIG. 15—*Effect of gas purges on corrosion of sensitized Type 316 steel in boiling copper sulfate-sulfuric acid solution with Allihn condenser. Solutions: 15.7 percent sulfuric acid, 5.7 percent anhydrous copper sulfate, with metallic copper. Specimens: 0.053 percent carbon, EW-6, heated 1 h at 677°C.*

low-oxygen, Allihn condenser system with nitrogen is without effect on intergranular attack (Fig. 15). The dot on the nitrogen curve is taken from Fig. 11 which is for the test without purging. Also, in this low-oxygen system, there is no difference between the no-contact and the copper-contact tests. Purging this system with air has essentially no effect on the copper contact test but, as expected, lowers the rate of intergranular attack in the copper-no-contact test. In the latter system, the corrosion potential of the stainless steel is higher (more noble) than that of the copper specimen.

In the normally high-oxygen finger condenser apparatus, purging with nitrogen reduces the oxygen concentration and consequently increases the rate of intergranular attack to that in the Allihn condenser (Fig. 16). There still is a small difference between the no-copper-contact and the copper-contact tests, indicating that not all oxygen was removed by the nitrogen purge. Purging the high-oxygen, finger condenser system with additional air lowers the rate of the copper-contact specimen from 2.1 to

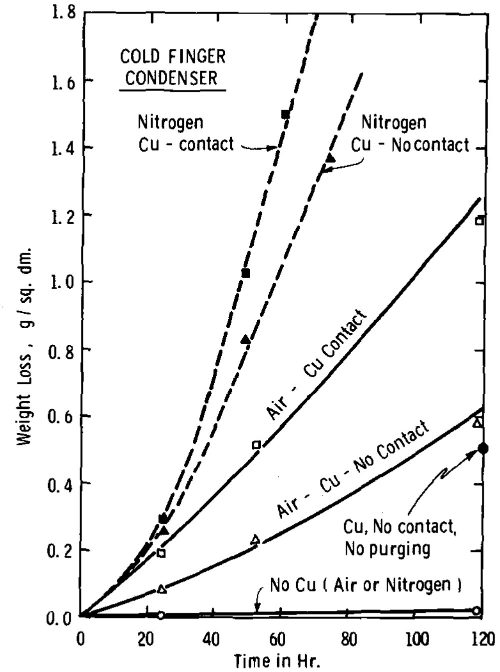

FIG. 16—*Effect of gas purges on corrosion of sensitized Type 316 steel in boiling copper sulfate-sulfuric acid solution with cold finger condenser. Solutions: 15.7 percent sulfuric acid with 5.7 percent anhydrous copper sulfate, with metallic copper. Specimens: 0.053 percent carbon, EW-6, heated 1 h at 677°C.*

1.2 g/dm^2 in 120 h (Fig. 8 for the no-purge test) and the copper-no-contact test by a small amount. Thus, increasing the supply of oxygen above that supplied by the cold finger increases the passivity of the stainless steel.

These tests on both copper and sensitized stainless steels show clearly that there is more oxygen present in the cold finger than in the Allihn apparatus. This is unexpected because the Allihn condenser is open to the air. However, the finger condenser provides a relatively large surface for a thin film of cold condensate which absorbs oxygen from the available air before dripping into the solution. A detailed investigation of this phenomenon is to be published in *Corrosion.*

Copper Sulfate-50 Percent Sulfuric Acid Test

Another method for increasing the rate of attack in the copper sulfate test is to increase the concentration of sulfuric acid in this solution. A 50 percent solution was used in 1964 [*30*] in connection with an investigation of intergranular attack in Type 321 alloys. Together with metallic copper, this solution provides such rapid attack on austenitic stainless steels that weight loss measurements can be used to evaluate the results in place of examination for fissures on specimens bent after testing. It also provides for interesting comparisons with results obtained in 50 percent sulfuric acid solutions containing ferric sulfate. As expected, this solution does not detect sigma-phase in Types 316 and 316L steels nor in titanium-stabilized 18Cr-8Ni (Type 321) stainless steel [*30*]. The latter may form sigma-phase which is readily detected in the nitric acid test, as is sigma-phase in Types 316 and 316L steels. However, unlike the latter steels, sigma-phase in Type 321 heats also increases somewhat the rate of corrosion in the ferric sulfate test.

As in the case of the copper sulfate test with 15 percent sulfuric acid, tests with 50 percent acid should be carried out with an Allihn condenser to provide rapid attack on sensitized stainless steel and to minimize corrosion of the metallic copper.

To date, the main application of the copper sulfate test with 50 percent sulfuric acid has been on the new ferritic stainless steels. This is discussed later in the paper.

Current ASTM Standards on Intergranular Corrosion Tests for Stainless Steels and Related Alloys

Austenitic Stainless Steels

At the time of the ASTM symposium [5] in 1949, only the boiling 65 percent nitric acid test, A 262, had been included in the ASTM standards. Even though this test was developed originally for evaluation of ferritic, iron-chromium, alloys, its scope is currently described as limited to austenitic stainless steels. This is also the case for all the other tests now in A 262. Thus, for the last 20 years, there has been no ASTM test whose scope included the ferritic stainless steels, such as Types 430 and 446.

The oxalic acid etch test was introduced in 1952, during a period of high and urgent production of austenitic stainless steels. This led to its rapid inclusion in A 262 as a method for screening specimens from the nitric acid test. In 1955, the copper sulfate, 16 percent sulfuric acid test, *without* metallic copper, was standardized for austenitic stainless steels. However, for this test, a separate standard, A 393, was established.

Thirteen years later, the ferric sulfate-sulfuric acid and the nitric-hydrofluoric acid tests were incorporated in A 262 as Practices B and D. Finally the quantitative work [*16,26*] on the effect of metallic copper in the copper sulfate-16 percent sulfuric acid test led to the inclusion in A 262 of this method as Practice E in 1970. On the basis of extensive correlations [*17,18,20,22,30-33*] between oxalic acid etch structures and performance in the various evaluation tests, it became possible to use this screening method on a selective basis for all four quantitative, hot acid corrosion tests in A 262.

There were then two standard test methods for copper sulfate-16 percent sulfuric acid tests, one (A 393) of very low sensitivity without metallic copper and the other with metallic copper, Practice E in A 262, whose sensitivity in detecting susceptibility to intergranular attack was essentially like that of the other practices in A 262. Later, this discrepancy was eliminated by the removal of A 393 from the *Book of ASTM Standards.*

However, in 1974, the old A 393 test was reinserted in the *Book of ASTM Standards* as ASTM Recommended Practice for Detection of Susceptibility to Intergranular Corrosion in Severely Sensitized Austenitic Stainless Steel (A 708-74) with 6 percent copper sulfate, 16 percent sulfuric acid, and a boiling period of 72 h without metallic copper. This reversal took place in response to a demand in the nuclear industry "for detection of susceptibility to intergranular corrosion of severely sensitized austenitic stainless steels." Of course, all the other tests previously described also detect cases of severely sensitized austenitic stainless steels. What was wanted was a relatively *insensitive* test which detects *only* cases of severe sensitization. Corrosion rates in this test without metallic copper are also dependent on the type of condenser used. Data in Table 4 on severely sensitized Type 304 specimens show much higher rates of intergranular attack in the flask fitted with an Allihn condenser than in the flask with the cold finger condenser. The type of condenser to be used is not now specified in A 708.

Current ASTM evaluation tests for detecting susceptibility to intergranular attack are outlined in Table 5. All the tests in A 262 are also included in American National Standard G 81.5 and have been approved for use by agencies of the Department of Defense (DOD) and for listing in the DOD Index of Specifications and Standards.

Nickel-Rich, Chromium-Bearing Alloys

An alloy of 54 percent nickel-15 percent chromium-15 percent molybdenum (Hastelloy Alloy C[5]) has been used frequently in severely corrosive environments for which the corrosion resistance of the austenitic stainless steels has proven inadequate. While it was known that the corrosion resistance of this alloy may be affected adversely by improper heat treatments, there was no rapid and reliable method for detecting such damage. In a detailed investigation [*34*] of the relationship of structures on the corrosion resistance of Alloy C and, later, of its low-carbon, low-silicon successor, Alloy C-276 [*35,36*], it was found that two kinds of molybdenum-rich precipitates may form during certain thermal exposures in the range of 649 to 1204°C (1200 to 2200°F). One is a molybdenum carbide and the

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[5] Trademark, Cabot Corporation, Kokomo, Ind.

TABLE 5—*ASTM evaluation tests for detecting susceptibility to intergranular attack.*[a]

Designations	Test Media	Alloys	Evaluation Criteria
A 262 Practice			
A	oxalic acid etch	304, 304L, 316, 316L, 317, 317L, 321, 347 casting alloys	yes
B	$Fe_2(SO_4)_3$-50% H_2SO_4	same	no
C	HNO_3	same	no
D	HNO_3-HF	316, 316L, 317, 317L	yes
E	$CuSO_4$-16% H_2SO_4 (Cu; contact)	austenitic stainless steels	yes
A 708 (old A 393)	$CuSO_4$-16% H_2SO_4 (no Cu)	austenitic stainless steels	yes
G 28	$Fe_2(SO_4)_3$-50% H_2SO_4	Hastelloy alloys C-276, G Carpenter 20 Cb-3 Inconel Alloys 600, 625 Incoloy Alloys 800, 825	no
G 35	polythionic acids (stressed specimen)	stainless steels (Ni-Fe-Cr alloys)	yes

[a] 1976 Annual Book of ASTM Standards, Part 10.

other a molybdenum-rich intermetallic compound, mu-phase. Even though these alloys contain 15 percent chromium, no chromium carbides have been detected. In many heats of Alloy C, the molybdenum-rich precipitates result in two maxima in corrosion rates (Fig. 17), one at 704°C (1300°F) and the other at 1033°C (1900°F). The lower maximum is associated primarily with the presence of a fine molybdenum carbide precipitate at grain boundaries. Near the maximum at 1033°C, relatively large particles of mu-phase are formed surrounded by relatively large carbide particles.

Increases in molybdenum content reduce the corrosion rate in reducing acids and increase the rate in oxidizing acids [*35-37*]. Thus, because there is severe depletion of molybdenum around the molybdenum carbide precipitates, their presence leads to severe intergranular attack in boiling 10 percent hydrochloric acid (Fig. 17) as well as in sulfuric acid solutions. The narrow grooves formed at grain boundaries by attack on the depleted zones are widened by the relatively high rate of general or grain-face corrosion in these acids. In contrast, the narrow grooves formed by direct attack on the fine molybdenum-rich carbide particles precipitated near 704°C are not readily widened in boiling 10 percent chromic acid because its rate of grain-face attack is low (Fig. 17). However, preferential attack by chromic acid on the large mu-phase particles and carbides formed near 1033°C leads to wide grooves, rapid undermining of grains, and high corrosion rates.

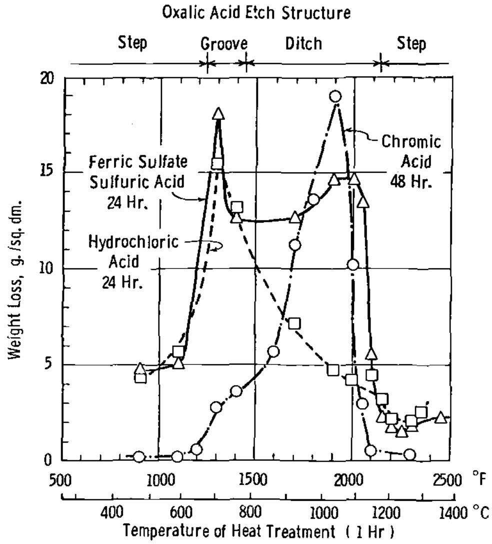

FIG. 17—*Effect of heat treatment on corrosion and etch structures of Hastelloy Alloy C* [34]. *Solutions: boiling 50 percent sulfuric acid with 42 g/litre ferric sulfate; boiling 10 percent hydrochloric acid; boiling 10 percent chromic* (CrO_3) *acid; specimens: 0.06 percent carbon.*

In the oxidizing ferric sulfate-50 percent sulfuric acid solution, both maxima are readily revealed because the molybdenum-rich carbide and mu-phase are attacked directly, and the resulting ditches are then enlarged by general corrosion in the concentrated acid. Grains are rapidly undermined and dislodged even when they are surrounded only by the very fine carbide precipitates formed at 704°C (1300°F). From Fig. 17, it is apparent why the ferric sulfate-50 percent sulfuric acid test was proposed [*30*] in 1963 as an evaluation test for Alloy C. It detects impairment in resistance to intergranular attack associated with both carbide and mu-phase precipitates in a readily measurable manner in only 24 h. The high molybdenum content (15 percent) of Alloy C and its somewhat lower (15 versus 18 percent chromium) chromium content result in a tenfold increase in the rate of general corrosion in the oxidizing ferric sulfate test for Alloy C as compared with austenitic, 18Cr-8Ni stainless steel. This is the reason why the test period for Alloy C (24 h) is so much shorter than that for austenitic stainless steels (120 h). Figure 17 also shows that oxalic acid etch structures can be correlated with susceptibility to intergranular attack.

The availability of an evaluation test procedure facilitated improvements in Alloy C. The carbon content was reduced to 0.02 percent maximum. By also reducing the silicon content to a maximum of 0.08 percent, the tendency towards formation of mu-phase was minimized. The effect of these changes on corrosion rates in the ferric sulfate test are shown in Fig. 18. Progressive reductions in the concentration of carbon from 0.08 to 0.004 percent first reduce the corrosion rates and then narrow the range of temperature of heat treatments causing intergranular attack. Increases in corrosion rates resulting from heat treatments of the 0.004C alloy are essentially a result of the presence of mu-phase. Because molybdenum depletion around this phase is relatively small, there is only a small effect of this phase on corrosion in reducing acids, such as hydrochloric acid.

Increasing use of other nickel-rich alloys in the process industries led to a need for evaluation methods for Inconel Alloys 600 and 625, Incoloy Alloys 800 and 825,[6] Hastelloy Alloy G, and Carpenter 20 Cb-3.[7] M. H. Brown [*38*] demonstrated that the ferric sulfate test can be also used to evaluate these alloys for susceptibility to intergranular attack. Following a series of comparison tests by an ASTM Task Group, ASTM Standard for Detecting Susceptibility to Intergranular Attack in Wrought Nickel-Rich, Chromium-Bearing Alloys (G 28-72) was established in 1972 (Table 5).

Stress-Corrosion Cracking in Polythionic Acids

This stress-corrosion test for austenitic stainless steels and related alloys is included in this discussion (Table 5) because cracking in polythionic

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[6] Trademark, The International Nickel Company, Huntington, W. Va.

[7] Trademark, Carpenter Technology Corporation, Reading, Pa.

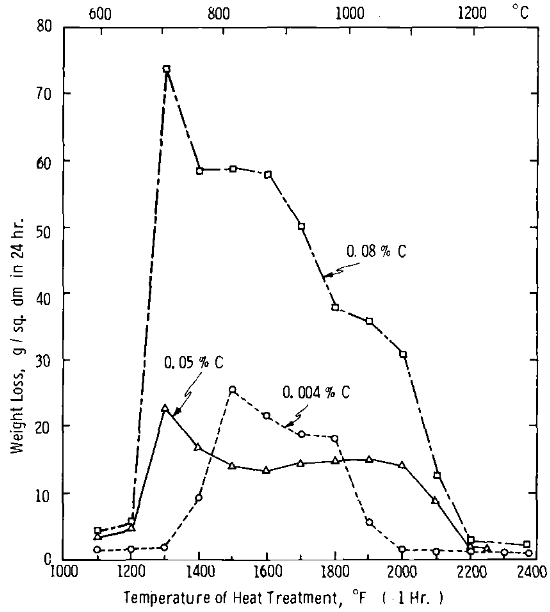

FIG. 18—*Effect of carbon content in Ni-Cr-Mo alloys on corrosion in the ferric sulfate-50 percent sulfuric acid test* [36].

acids occurs only on sensitized alloys. Polythionic acids, $H_2S_{3-5}O_6$, can form readily in petroleum refinery units during shutdown by the interaction of sulfides, oxygen, and moisture. A. Dravnieks and C. H. Samans [*39*] reported in 1957 that sensitized 18Cr-8Ni stainless steels fail by intergranular cracking. Later investigators [*40,41*] demonstrated that Inconel Alloy 600 also cracks in this environment when severely sensitized. In this alloy, the carbide is Cr_7C_3 [*41*]. In both the 18Cr-8Ni stainless steel and in Alloy 600, susceptibility to cracking can be prevented by heating the alloys for 4 h at 871°C (1600°F) and thereby diffusing some chromium into the chromium-depleted zones around the particles of chromium carbide precipitate. From this, it has been concluded [*40,41*] that susceptibility to intergranular cracking is caused by chromium-depleted zones and not by the chromium carbide particles themselves.

In the laboratory, polythionic acid is made by first passing sulfur dioxide and then hydrogen sulfide into water [*40*]. This procedure has been adopted in ASTM Recommended Practice for Determining the Susceptibility of Stainless Steels and Related Nickel-Chromium-Iron Alloys to Stress Corrosion Cracking in Polythionic Acids (G 35-73). Intergranular cracking takes place on sensitized Type 304 U-bends in this relatively mild environment at room temperature in less than an hour (Fig. 19), and on Alloy 600

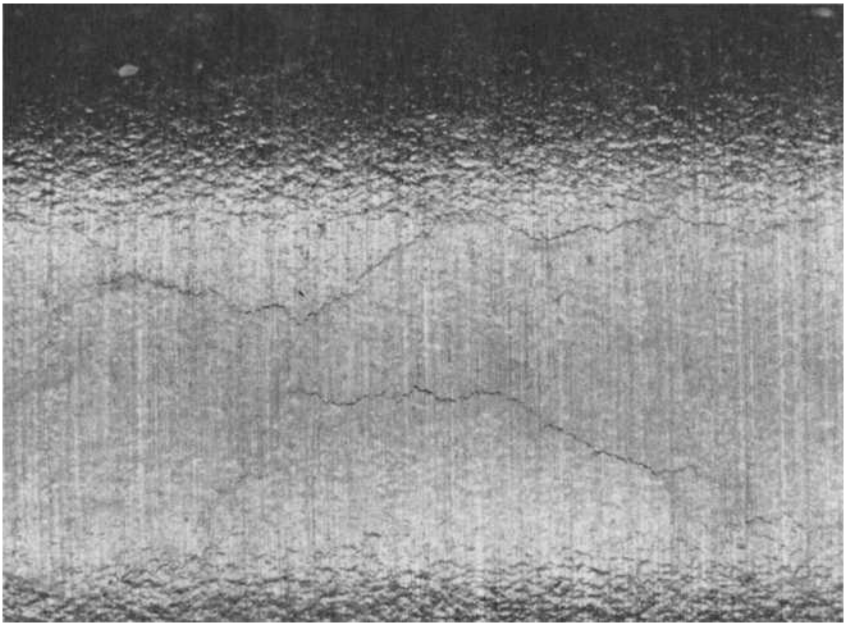

FIG. 19—*Stress-corrosion cracking of sensitized Type 304 steel in polythionic acid (×16). Solution: distilled water saturated with hydrogen sulfide and sulfur dioxide at 25°C. Specimen: Type 304 steel heated 2 h at 677°C. Appearance after 1 h of exposure in the solution.*

in 20 to 300 h depending on the severity of sensitization (Fig. 20). In cases of very severe sensitization, the attack becomes more like stress-accelerated intergranular corrosion than intergranular stress corrosion cracking (Fig. 21).

New Standard Test Methods for Ferritic Stainless Steels

As indicated previously, the current ASTM evaluation tests of Table 5 do not apply specifically to ferritic stainless steels, such as Types 430 and 446, that is, these are not mentioned under the "Scope" sections of the standards. The tests in A 262 have, of course, been used for iron-chromium alloys but primarily for research and alloy development. Recent investigations on Types 430 and 446 [*42*] and the introduction of new iron-chromium-molybdenum alloys have emphasized the need for a separate group of test methods for these alloys.

Figures 22 and 23 provide a comparison of three acid corrosion tests on Types 430 and 446 specimens sensitized at various temperatures. In the iron-chromium alloys, diffusion of both carbon and nitrogen is much more rapid than in austenitic 18Cr-8Ni stainless steels. Water quenching

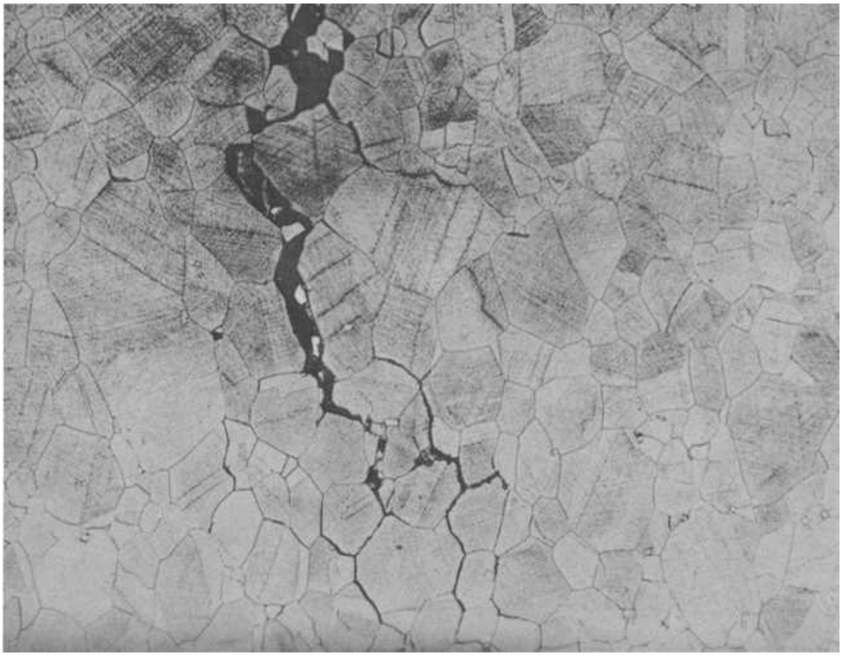

FIG. 20—*Stress corrosion of sensitized Inconel Alloy 600 in polythionic acid* (×*200*). *Solution: distilled water saturated with hydrogen sulfide and sulfur dioxide at 25°C. Specimen: heated 1h at 704°C. Cracked between 264 and 384 h of exposure to solution.*

from temperatures above the precipitation range, 430 to 930°C, does not prevent precipitation of chromium carbides and nitrides. Nitrogen forms β-(Cr, Fe)$_2$ N [*42,43*], which also causes chromium depletion. It is of importance in commercial heats of Type 446 steel because they contain about 0.2 percent nitrogen to reduce the grain size and facilitate hot working. The rapid diffusion of interstitial elements makes it impossible to prevent susceptibility to intergranular attack by solution annealing Types 430 and 446 alloys above 930°C. Instead, advantage is taken of the high rate of diffusion of chromium in the iron-chromium system. By heating these alloys near 790°C, chromium-depleted zones surrounding the chromium carbide and nitride precipitates are readily replenished even though this temperature falls within the carbide and nitride precipitation range. The result is a structure which contains these precipitates but which is resistant to intergranular attack.

Figure 22 shows that, for Type 430 (17 percent chromium) steel, the ferric or cupric sulfate tests with 50 percent sulfuric acid provide a clearer measure of susceptibility to intergranular attack in 24 h than does the 240-h nitric acid test. This difference is even greater for the higher chro-

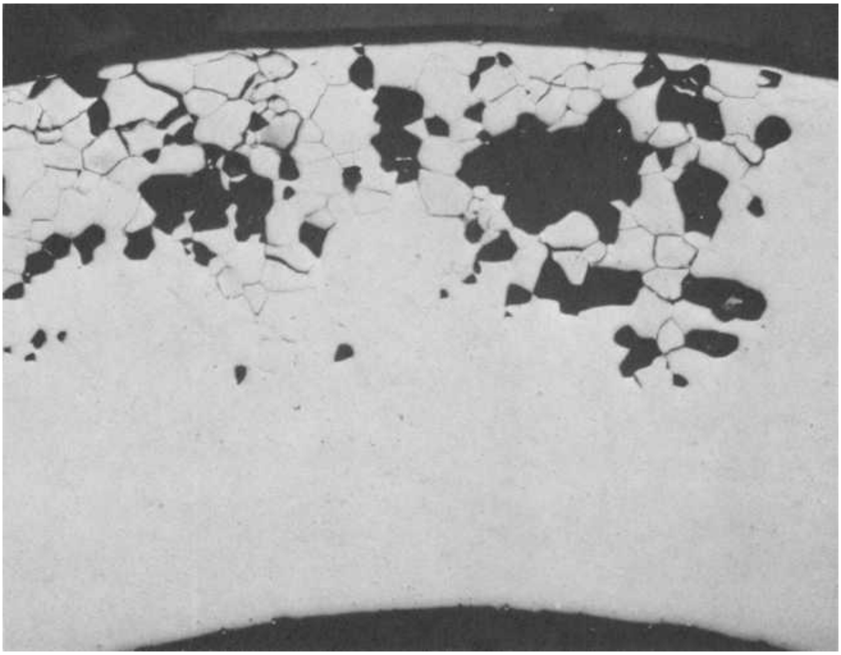

FIG. 21—*Corrosion of sensitized and stressed Inconel Alloy 600 in polythionic acid (×40). Solution: distilled water saturated with hydrogen sulfide and sulfur dioxide at 25°C. Specimen: heated 100 h at 600°C. Exposed 19 h in polythionic acid at 25°C.*

mium, Type 446 (25 percent chromium) steel (Fig. 23). The nitric acid test is a relatively insensitive method for detecting susceptibility to intergranular attack in this alloy.

The need for increased resistance in stainless steels to chloride stress corrosion cracking and to pitting and crevice corrosion, together with the introduction of several new processes for reducing the carbon and nitrogen contents, has led to the development of several new stainless steels based on the iron-chromium-molybdenum system. Table 6 contains a list of five of the new iron-chromium-molybdenum alloys. They fall into two groups, high-purity alloys with low carbon and nitrogen contents and stabilized alloys whose carbon plus nitrogen contents range from 500 to 800 ppm. The new process used to refine the stabilized alloys, argon-oxygen decarburization, is lower in cost than that of vacuum induction melting which is required for the high-purity alloys. The development and properties of these alloys are described in the references given in Table 6 and have been recently summarized and interpreted by R. F. Steigerwald [*44*] and M. A. Streicher [*37*].

Because of the resistance of the iron-chromium-molybdenum alloys to stress-corrosion cracking in chloride solutions, they can provide a large

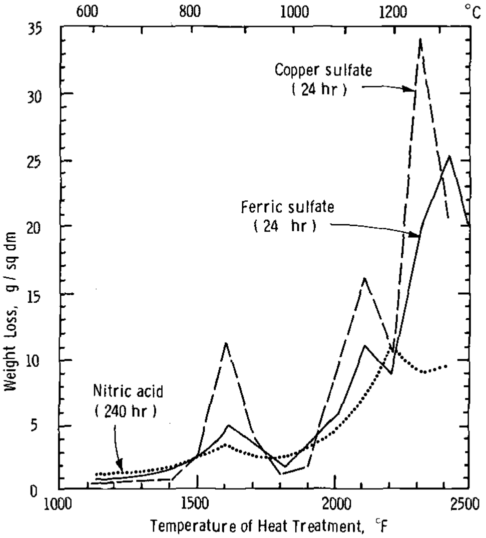

FIG. 22—*Effect of heat treatment on corrosion of Type 430 steel in boiling solutions* [42]. *Heat treatments—1 h as shown, water quenched. Nitric acid—65 percent. Ferric sulfate—50 percent sulfuric acid with ferric sulfate. Copper sulfate—50 percent sulfuric acid with copper sulfate and metallic copper not in contact with specimen.*

part of the practical solution to the chloride stress-corrosion cracking problem. In addition, depending on their alloy content, they provide resistance to pitting and crevice corrosion in chloride solutions ranging from that roughly equivalent to Types 430, 446, and 304 steels for the 18Cr-2Mo-Ti alloy to that equivalent in some cases to the costly Hastelloy Alloys C and C-276 and titanium for the 29Cr-4Mo alloys. The latter alloys are also among the few alloys which have been found to be resistant to crevice corrosion during immersion in the ocean.

Thermal exposures during welding or during heat treatments may form chromium carbides and nitrides in the iron-chromium-molybdenum alloys. However, carbon can be held to the range of 30 to 60 ppm in the vacuum induction process and to 20 ppm in the electron-beam refining process. As a result, there is no significant precipitation of chromium carbides during welding. The rate and amount of precipitation of chromium nitride depend not only on the concentration of nitrogen, but also on the molybdenum content. Thus, among the high-purity alloys, 26 percent chromium-1 percent molybdenum and 29 percent chromium-4 percent molybdenum, the alloy with the higher molybdenum content may contain as much as 200 ppm (0.020 percent) nitrogen (Footnote 10 on p. 37, [52]), whereas in the 26Cr-1Mo alloy without niobium, 90 ppm make weldments subject to intergranular attack [*44,52*]. This difference is of industrial importance

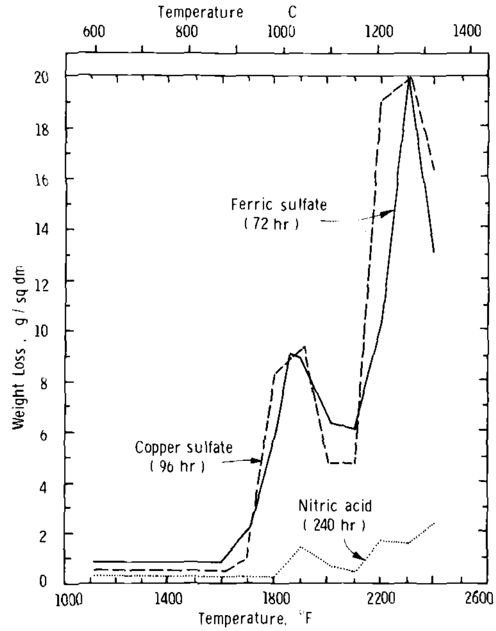

FIG. 23—*Effect of heat treatment on corrosion of Type 446 steel in boiling acid solutions* [42]. *Heat treatments—1 h as shown, water quenched. Nitric acid—65 percent. Ferric sulfate—50 percent sulfuric acid with ferric sulfate. Copper sulfate—50 percent sulfuric acid with copper sulfate and metallic copper not in contact with specimen.*

because nitrogen can be reduced to about 110 ppm by melting in vacuum induction equipment but is difficult and costly to reduce below this concentration. Thus, such equipment can meet the requirements for nitrogen in the 29Cr-4Mo alloy (200 ppm max) but not those for the 26Cr-1Mo alloy as determined by corrosion testing of weldments.

In recent years, niobium has been added in small (0.05 to 0.08 percent) amounts to the high-purity, electron-beam melted 26Cr-1Mo alloy (as made by the Vacuum Metals Division of Airco, Inc.) to reduce susceptibility to intergranular attack caused by the presence of about 0.01 percent nitrogen. However, this concentration is insufficient to make this alloy resistant to intergranular attack after sensitizing heat treatments [*37*]. It is less resistant after such heat treatments than the less pure, titanium-stabilized alloy III of Table 4. To overcome this problem the new producers of this alloy, Allegheny Ludlum Steel Corp., have increased the niobium content to 0.100 percent. They are making this alloy by vacuum induction melting. This relatively small addition of niobium apparently does not result in the type of preferential attack observed in oxidizing solutions on stabilized alloys with higher niobium or titanium concentrations described later in this section.

TABLE 6—*New ferritic stainless steels* [37].

Alloy Composition, % by weight		Limits for Carbon and Nitrogen	Refining Processes	References
I	Fe-18Cr-2Mo-Ti	C—0.0250% max N—0.0250% max C + N < 0.030% desirable Ti + Nb = 0.20 + 4 (C + N) min = 0.80 max	argon-oxygen decarburization or vacuum oxygen decarburization	[*44-47*][8]
II	Fe-26Cr-1Mo (Nb)	C—0.0050% max N—0.0150% max Nb = 0.07% (EB) Nb = 0.100% (VI)	electron beam hearth refining (previous method) Vacuum induction melting (present method)	[*37,48,49*]
III	Fe-26Cr-1Mo-Ti	C—0.0400% max N—0.0400% max 0.2 to 1.0% Ti C + N = 0.50 typical	argon-oxygen decarburization	[*50,51*][9,10]
IV	Fe-29Cr-4Mo	C—0.0100% max N—0.0200% max C + N = 0.0250% max	vacuum induction	[*52-54*][10]
V	Fe-29Cr-4Mo-2Ni	same	same	

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[8] Dundas, H. J. and Bond, A. P., this publication, pp. 154-178.

[9] Sweet, A. J., this publication, pp. 197-232.

[10] Nichol, T. J. and Davis, J. A., this publication, pp. 179-196.

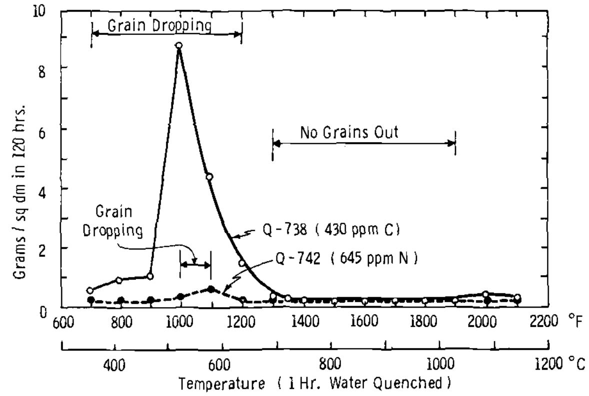

FIG. 24—*Effect of heat treatment on intergranular corrosion of Fe-29Cr-4Mo alloy. Specimens: heat treatment 1 h as shown, water quenched. 2.5 by 2.5 by 0.2 cm. Q-738: 40 ppm N; Q-742: 120-ppm carbon. Solution: boiling ferric sulfate-50 percent sulfuric acid.*

The effect of molybdenum on precipitation of nitrides and carbides is illustrated in Fig. 24 for two 29Cr-4Mo alloys containing carbon and nitrogen greatly in excess of the maximum concentrations specified for this alloy, Table 6. In contrast to the effect of heat treatments in molybdenum-free iron-chromium alloys, Figs. 22 and 23, heat treatments of both the high-carbon and high-nitrogen compositions above 700°C do not result in sensitization. Precipitation in the 29Cr-4Mo composition is slow enough so that water quenching through the sensitizing range does not result in susceptibility to intergranular attack. This is similar to the behavior of *austenitic* stainless steels. Only direct heating in the sensitizing range (370 to 700°C for chromium carbide and 540 to 650°C for chromium nitride) produces sensitization. For the carbide, the temperature of the most rapid rate is near 540°C and for the nitride near 600°C. Note that the effect of carbon is much greater than that of nitrogen. The maximum ratio of rate of the sensitized to the rate of the annealed specimens is 44.5 for the high-carbon versus 3.0 for the high-nitrogen heat. Thus, for the high-molybdenum alloys, 29 percent chromium-4 percent molybdenum and 29 percent chromium-4 percent molybdenum-2 percent nickel, the response to heat treatment is similar to that of the austenitic stainless steels, while that of the low-molybdenum, 26 percent chromium-1 percent molybdenum, alloy is more like that of the iron-chromium alloys, such as Type 446.

Intermetallic compounds may also be formed in the iron-chromium-molybdenum alloys. For the 29Cr-4Mo and 29Cr-4Mo-2Ni compositions, the temperature of most rapid formation is 816°C (1500°F) [*53*]. A small amount of sigma-phase is formed (Fig. 25) after a 1-h heat treatment at this temperature. Its presence does not impair resistance to intergranular attack in the oxidizing ferric sulfate test (Fig. 24), but it does reduce the

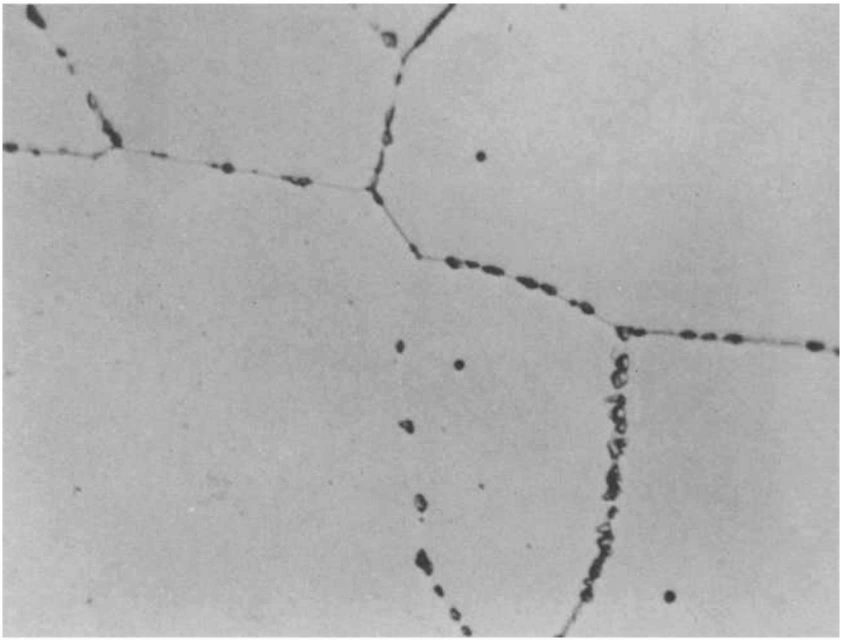

FIG. 25—*Sigma-phase in Fe-29Cr-4Mo alloy* [53] (×*1000*). *Heated 1 h at 816°C, water quenched. Etched electrolytically in 10 percent sulfuric acid.*

toughness of the alloy somewhat [*54*]. Heating a specimen for 100 h at 816°C produces large amounts of chi- and sigma-phases (Fig. 26). Analysis by X-ray fluorescence showed that the chi-phase is rich in molybdenum and chromium and that, in the small amount of sigma-phase within the chi-phase, there is even greater enrichment of these elements. Nevertheless, apparently because of the high-chromium content, there is no intergranular attack on this alloy in a 120-h test in the ferric sulfate-50 percent sulfuric acid solution. Solution annealing at 1040°C readily dissolves these phases.

Carbon and nitrogen in the lower chromium and molybdenum 26Cr-1Mo and 18Cr-2Mo alloys can be stabilized by addition of titanium and niobium without a significant loss in ductility. Therefore, they can be refined by the argon-oxygen decarburization (AOD) process, in which carbon plus nitrogen can be reduced to the range of 250 to 800 ppm (Table 6). The amount of stabilizing element added during melting must be balanced between the minimum needed to combine rapidly with carbon and nitrogen and, thereby, prevent the formation of chromium carbides and nitrides during cooling of a weldment and the need to prevent unnecessary losses in toughness by excess concentrations. At least double the theoretical

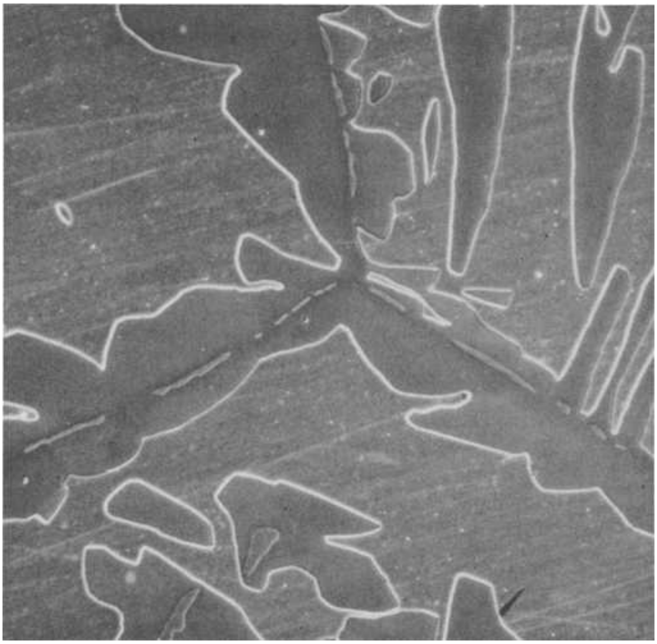

FIG. 26—*Chi- and sigma-phases in Fe-29Cr-4Mo-2Ni alloy (SEM ×800). Heated 100 h at 816°C, water quenched. Etched electrolytically in 10 percent sulfuric acid. Fine particles in grain boundaries are sigma-phase, and large bands are chi-phase. Specimen cracked on bending.*

concentration of titanium required to combine with all of the carbon plus nitrogen must be added to prevent carbide and nitride sensitization. Titanium reduces the toughness of the alloys, that is, raises the transition temperature, and excess amounts promote the formation of intermetallic phases. As in the case of invisible sigma-phase in Type 316L steel, these phases have not yet been observed directly in the microstructures. Only their deleterious effects on properties have been measured.

Their presence in 18Cr-2Mo-Ti and 26Cr-1Mo-Ti alloys makes these compositions subject to intergranular attack not only in the nitric acid test, but also in the ferric sulfate test [*53,55*]. In this respect, they differ from the behavior of such phases or grain boundary alloy segregation phenomena in Types 316L and 316 steels (Table 2) which are subject to preferential attack only in the nitric acid test. By prolonged heating of 26Cr-1Mo-Ti alloy in the range of 595 to 850°C, a phase rich in titanium, molybdenum, and silicon has been identified [*56*]. The appearance of this grain boundary effect in weldments of titanium-stabilized, iron-chrimium-molybdenum alloys has led to the recommendation that these alloys not be used in highly oxidizing environments for which their high chromium contents otherwise made them eminently suitable [*51*]. Investigations of these problems are reported in detail in several papers of this symposium (Footnotes 8–10).

Even in the as-received (unwelded, nonsensitized) condition, there is considerable attack on grain boundaries of stabilized alloys in the ferric sulfate test (Fig. 27). On 26Cr-1Mo-Ti alloy, there is progressive widening of the ditches at the boundaries but no undermining or dislodgment of grains. On 18Cr-2Mo-Ti alloy, there is dislodgment of grains even on as-received material (Fig. 28). In contrast, in the copper sulfate-50 percent sulfuric acid solution, even though there is also some attack at the boundaries of 26Cr-1Mo-Ti alloy, it does not progress beyond a shallow groove (Fig. 29).

Because they are preferentially attacked, the numerous titanium carbide and nitride particles in stabilized alloys also increase general corrosion rates in oxidizing acids.

A task group of ASTM Subcommittee A01.14 has used these findings

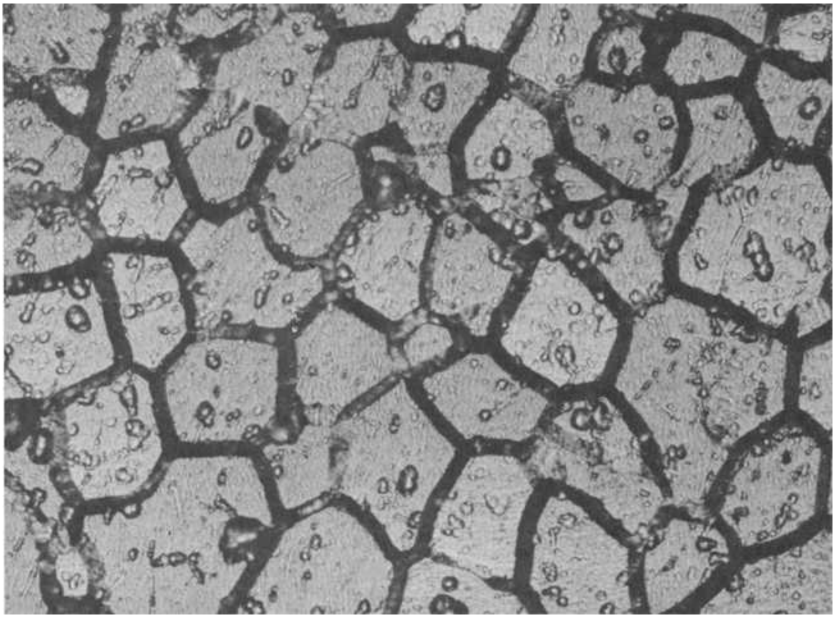

FIG. 27—*Corrosion of Fe-26Cr-1Mo-Ti alloy in ferric sulfate test* (×*500*). *Specimen: as-received condition after 104 h. Slow preferential attack at grain boundaries. Solution: boiling ferric sulfate-50 percent sulfuric acid.*

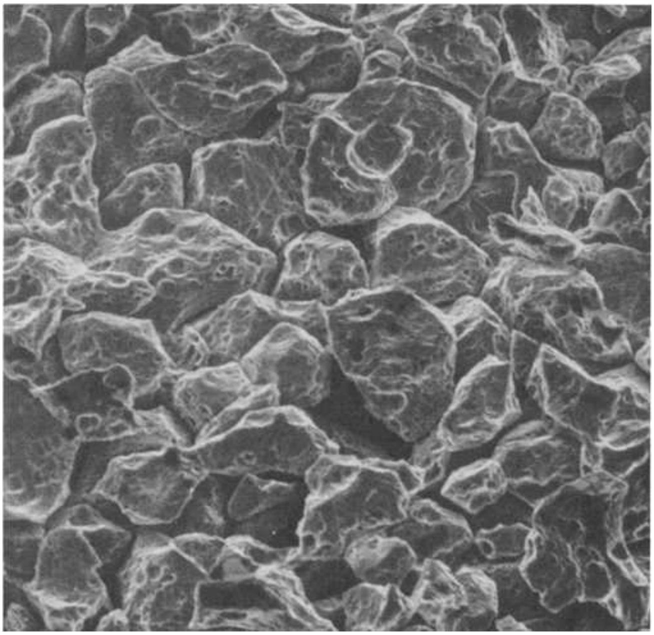

FIG. 28—*Corrosion of Fe-18Cr-2Mo-Ti alloy in ferric sulfate test (×600). Alloy in the as-received condition. Exposed in boiling ferric sulfate-50 percent sulfuric acid test. Scanning electron micrograph.*

on ferritic stainless steels to propose a combination of tests for evaluation of ferritic stainless steels. Table 7 contains a summary of their most recent test proposals. The ferric sulfate test is confined to unstabilized alloys, that is, the old ferritic stainless steels, Types 430 and 446, and the new low-carbon plus nitrogen, iron-chromium-molybdenum, alloys. Two versions of the copper sulfate-sulfuric acid test are included, the test with 16 percent acid for the 18Cr alloys and the 50 percent acid test for the 25 to 30Cr alloys. Other tests, such as the nitric and the nitric-hydrofluoric acid, were excluded to avoid duplication of methods which provide similar results and for other reasons to be discussed.

Still, for most of the alloys in Table 7, two tests are listed which provide the same results, that is, a measure of the susceptibility to intergranular attack associated with precipitates of chromium carbides and nitrides. Testing times, which are a function of the chromium content, are essentially the same for each alloy in both tests. The main difference is the method of evaluation for the 18Cr alloys in the copper sulfate-16 percent sulfuric acid solution. Of the three evaluation methods listed, only one, the examination for cracks on a specimen bent after testing, is applicable in this

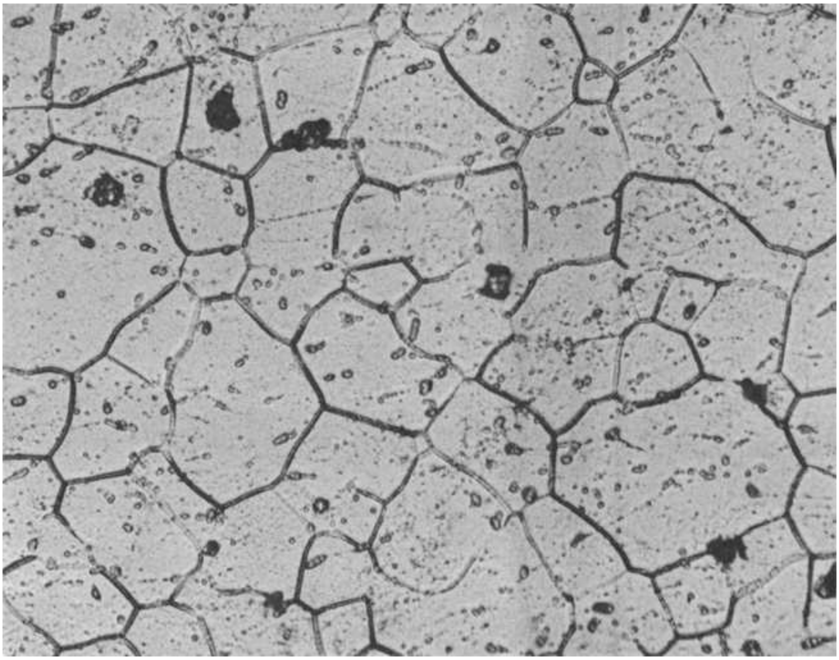

FIG. 29—*Corrosion of Fe-26Cr-1Mo-Ti alloy in copper sulfate test (×500). Specimen: as-received condition, exposed 116 h. Solution: boiling copper sulfate-50 percent sulfuric acid with metallic copper, Allihn condenser.*

test. The only exception is the Type 430 alloy which can be also tested in the ferric sulfate solution and then evaluated on the basis of weight loss.

Whenever more than one evaluation criterion is specified, the preferred method is indicated by superscript *d* in Table 7. Ideally, quantitative methods, such as corrosion rates based on weight loss measurements, for expressing the results of evaluation tests are preferred. However, on high-chromium alloys and when rapid results are desired in the copper sulfate-16 percent sulfuric acid test, the dislodgment of grains is so slow that weight losses are too small to serve as a criterion for susceptibility to intergranular attack. Also, during the development of the new iron-chromium-molybdenum alloys, susceptibility to sensitization was generally determined by testing of a welded coupon rather than by testing of an isothermally heated specimen, such as is customary with the austenitic alloys (A 262). In a weldment, intergranular attack may be confined to a narrow component, such as the weld metal or the heat-affected zone (Fig. 30). This also greatly reduces the possibility that a meaningful corrosion rate based on a weight loss measurement can be determined.

TABLE 7—*Evaluation tests for ferritic stainless steels.*[a] *(It is assumed that stabilized alloys will not be used in oxidizing solutions.)*

		Evaluation Criteria		
Alloy	Time of Test, h	Weight Loss	Microscopic Examination[b]	Bend Test[c]
PRACTICE (X) FERRIC SULFATE-50% SULFURIC ACID TEST				
430 (17Cr)	24	yes[d]	*yes*	*no*
446 (25Cr)	72	yes[d]	yes	no
26Cr-1Mo	120	yes	yes[d]	no
29Cr-4Mo	120	no	yes[d]	no
29Cr-4Mo-2Ni	120	no	yes[d]	no
PRACTICE (Y) COPPER SULFATE 50% SULFURIC ACID TEST				
446 (25Cr)	96	yes[d]	yes	no
26Cr-1Mo	120	yes	yes[d]	no
26Cr-1Mo-Ti	120	yes	yes[d]	no
29Cr-4Mo	120	no	yes[d]	no
29Cr-4Mo-2Ni	120	no	yes[d]	no
PRACTICE (Z) COPPER SULFATE-16% SULFURIC ACID TEST				
430 (17Cr)	24	no	no	yes
434 (17Cr-1Mo)	24	no	no	yes
436 (17Cr-1Mo-Nb)	24	no	no	yes
18Cr-Ti	24	no	no	yes
18Cr-2Mo-Ti	24	no	no	yes

[a] As proposed by a task group of ASTM Subcommittee A1.14, Chairman, R. F. Steigerwald, 30 Sept. 1977.

[b] Examination of specimen at ×40 for evidence of dislodged grains.

[c] Examination of specimen after testing for cracks (fissures) on specimen which has been bent 180 deg over a mandrel having a diameter equal to the thickness of the specimen being bent.

[d] The preferred criterion in cases for which more than one is applicable.

Only on Types 430 and 446, when tested in either of the 50 percent sulfuric acid solutions, is the weight loss large enough for it to be used as an evaluation criterion. Even for these cases, this method is confined to unwelded specimens.

For all other tests, visual criteria for evaluation must be used. One is examination for evidence of dropped grains. But, at present, the draft for the new method specifies that "the number of dropped grains per unit area that can be tolerated is subject to agreement between the purchaser and supplier." The other visual method consists of examining the specimens after testing and bending "180° over a diameter equal to the thickness of the specimen being bent." Because not all specimens can be bent, other methods must then be used.

As in other standard methods, the various practices specified in Table 7 for ferritic alloys were limited by the testing data available to the task group which demonstrated the validity of each combination of test method, alloy composition, and evaluation criteria shown. Some of these data, together with new results, are included in the papers of this volume.

Summary of the Action of Evaluation Test Solutions on Stainless Steels

To summarize the properties of various evaluation test solutions, the corrosion potentials of stainless steels are given in Table 8 along with the phases detected by each of the solutions. Data on the action of boiling 5 percent sulfuric acid have been added for comparison because, in this reducing solution, corrosion is by hydrogen evolution with a potential of −0.6 V versus SCE. On austenitic stainless steels, all of the test solutions detect susceptibility associated with chromium carbide precipitates. Sigma-phase, or its precursor, is detected only in the most oxidizing of the solutions, nitric acid, in which stainless steels have a corrosion potential of about +1.0 V versus SCE.

Chromium depletion caused by precipitation of chromium carbides and nitrides is detected in all test solutions except for iron-chromium alloys in boiling 5 percent sulfuric acid (Table 8). The reason for this difference in action of pure sulfuric acid on sensitized iron-chromium-nickel and

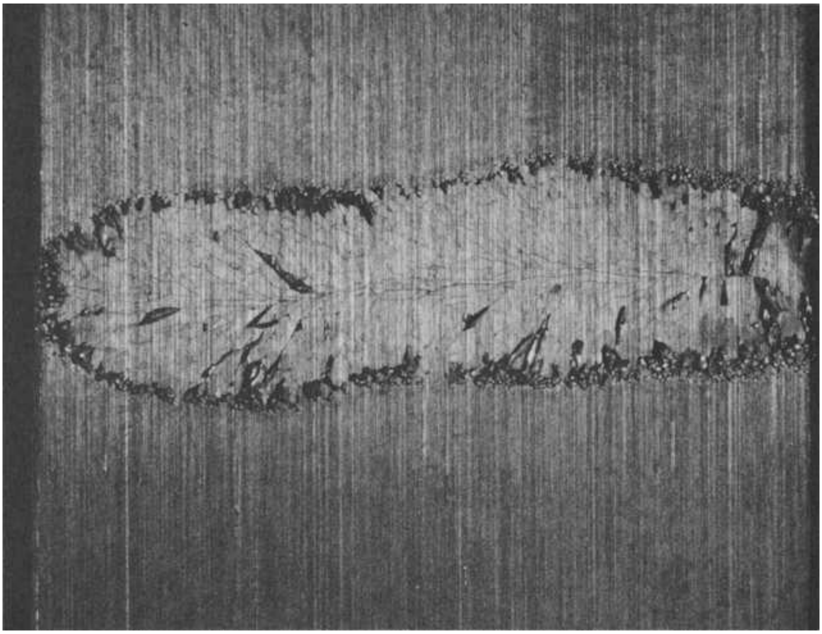

FIG. 30—*Intergranular attack on weldment in ferritic stainless steel caused by high nitrogen content* (×5). *Autogenous weld in 28.5Cr-4.2Mo alloy with 22-ppm carbon and 388-ppm nitrogen after exposure in ferric sulfate-50 percent sulfuric acid test.*

TABLE 8—*Corrosion potentials of wrought stainless steels in acid solutions.*

Electrode Potential (V) versus Saturated Calomel Electrode (SCE)			Precipitates and Phases Detected				
			Austenitic Steels		Ferritic Steels		
					Cr-Carbide and Nitride		Intermetallics
		Solutions	Cr-Carbide	Sigma	Fe-Cr	Fe-Cr-Mo	(Fe-Cr-Mo(Ti))
Passive (Noble) ↑	+1.0	←nitric acid, 65% (0.75 to 1.0 V during test)	yes	316, 321 316L, 317, 317L	yes	yes	yes
	+0.6	←ferric sulfate-sulfuric acid	yes	no[a]	yes	yes	yes[b]
	+0.35	←copper sulfate-sulfuric acid	yes	no	yes	yes	no[c]
	+0.1	←copper sulfate-sulfuric acid with metallic copper	yes	no	yes	yes	no
	0.0						
Active ↓	−0.1	←10% nitric-3% hydrofluoric acid (oscillates between +0.3 and −0.1 V)	yes	no	yes	yes	no
	−0.6	←5% sulfuric acid	yes	no	no	yes[c]	no[c]

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[a] There is some effect of sigma phase in Type 321 steel.

[b] In *un*stabilized Fe-Cr-Mo alloys (29Cr-4Mo and 29Cr-4Mo-2Ni) sigma- and chi-phases do not cause intergranular attack.

[c] Tests of this investigation. Other entries from previous literature.

iron-chromium alloys, both of which contain chromium carbide precipitates, is shown in Fig. 31. General corrosion was determined on two series of alloys in boiling 5 percent sulfuric acid, iron-chromium and Fe-10Ni-Cr alloys, both with increasing chromium contents. Increasing the chromium content of iron-chromium alloys actually leads to an increase in corrosion rate in this solution. Therefore, it would not be expected that chromium depletion at grain boundaries leads to intergranular attack in boiling 5 percent sulfuric acid. This is verified by the initial stage of attack on a sensitized Type 446 heat (Fig. 32). During longer exposures, the chromium carbide precipitate serves as an efficient cathode and causes some preferential attack adjacent to it. The result is a shallow groove.

In contrast, as the chromium content of Fe-10Ni alloys is increased, there is a rapid decrease in corrosion rate. Thus, it might be expected that a sensitized Type 304 steel with 18 percent chromium and about 10 percent nickel would be subject to intergranular attack in 5 percent sulfuric acid (Fig. 33). Finally, in the oxidizing ferric sulfate test, the corrosion rate of iron-chromium alloys also decreases with increasing chromium content, and, therefore, a sensitized Type 446 specimen is subject to intergranular attack (Fig. 34).

Sensitization by chromium carbide (and probably also nitride) precipitates in iron-chromium-molybdenum alloys is detected by all of the solu-

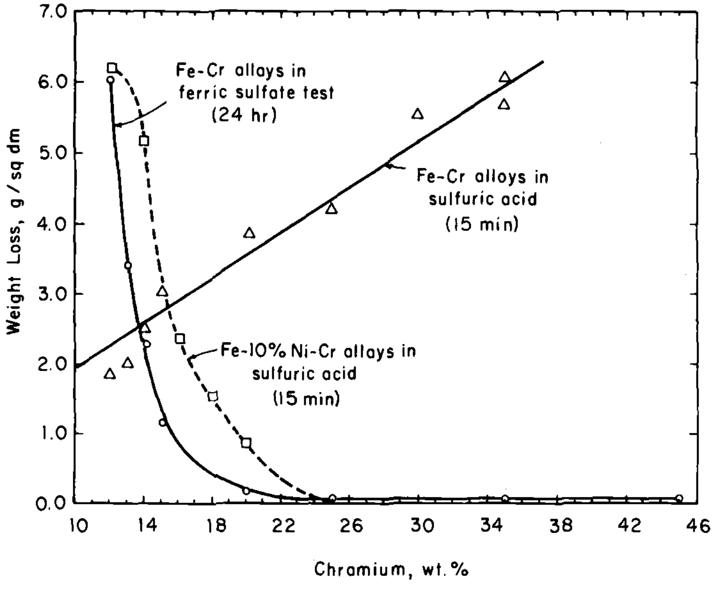

FIG. 31—*General corrosion of Fe-Cr and Fe-10Ni-Cr alloys in sulfuric acid solutions* [42]. *Ferric sulfate—boiling 50 percent sulfuric acid with 25 g/600 ml ferric sulfate. Sulfuric acid—boiling 5 percent acid.*

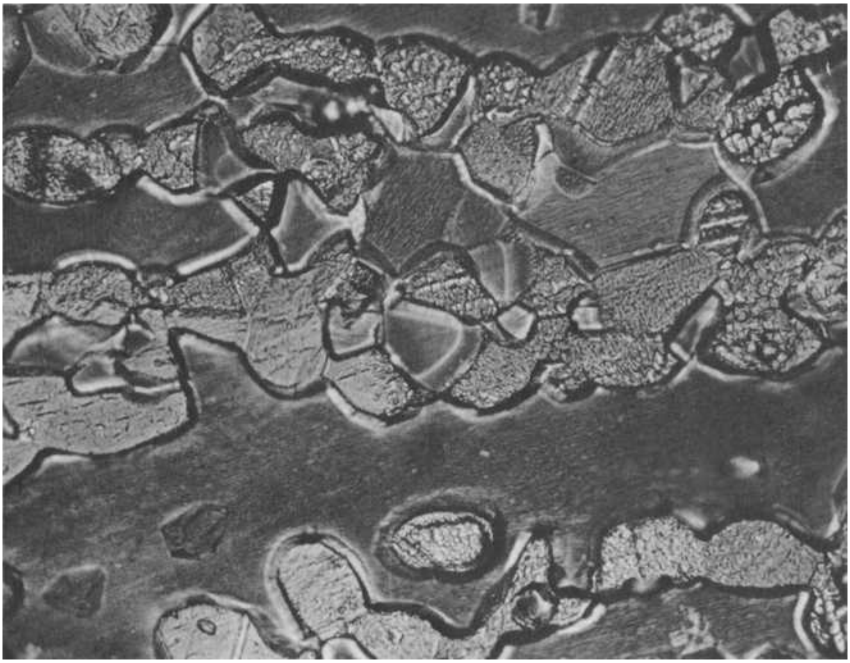

FIG. 32—*Initial attack of sulfuric acid on sensitized Type 446 steel (×500). Solution: boiling 5 percent sulfuric acid. Specimen: heated 1 h at 1150°C (2100°F), water quenched. Exposed 30 s. Preferential attack on austenite islands. No intergranular attack.*

tions for which data are available. This is also the case for improperly stabilized iron-chromium-molybdenum alloys. These may contain chromium carbides and nitrides either because of insufficient concentrations of titanium or niobium or because of inadequate stabilizing heat treatments.

Intermetallic (chi or sigma) phases, or their precursors in the forms of equilibrium segregation of alloying elements at grain boundaries in molybdenum-bearing austenitic alloys, result in intergranular attack in nitric acid solutions in which these steels have a corrosion potential of + 0.75 V versus SCE or greater. However, on ferritic iron-chromium-molybdenum alloys containing titanium (but not with niobium), there is attack in both the ferric sulfate and the nitric acid solutions. Thus, the intermetallic phases in iron-chromium-molybdenum alloys which are rich not only in molybdenum, but also in titanium and silicon, are more sensitive to oxidizing environments than those in Type 316L steel. (The small effect of titanium in Type 321 steel (Table 8) on the properties of sigmaphase also suggests that titanium enhances the susceptibility to attack on intermetallic phases [*30*].) Otherwise the effect of intermetallic phases is the same in the austenitic and ferritic stainless steels, that is, there is no preferential attack on these phases in

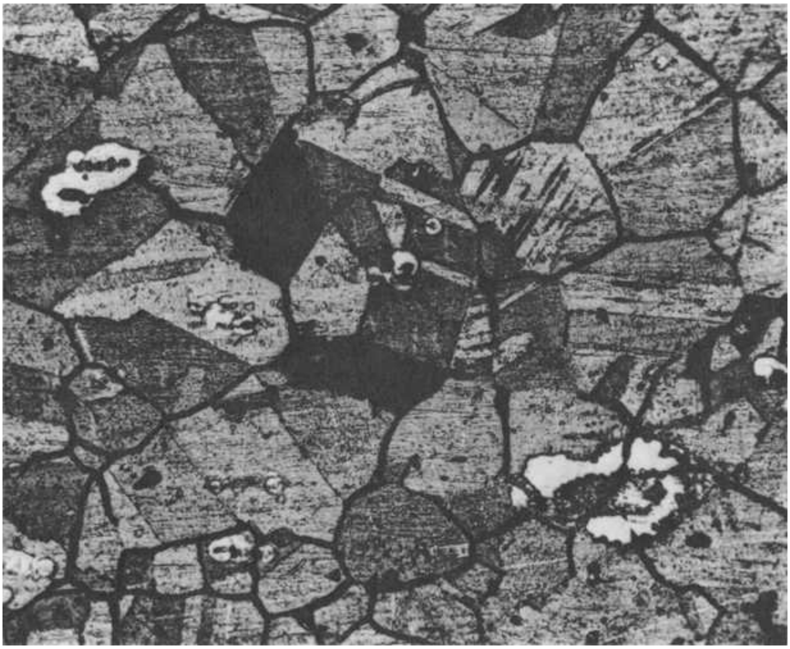

FIG. 33—*Intergranular attack on sensitized Type 304 steel in sulfuric acid* (×*250*). *Steel: heated 1 h at 677°C. Solution: boiling 5 percent sulfuric acid for 5 min.*

solutions in which the corrosion potentials are lower than +0.6 versus SCE.

Because there are no data on the effect of this process on corrosion in solutions in which the corrosion potential is between +0.1 (copper sulfate test with copper) and +0.6 V versus SCE (ferric sulfate test), the recommendations for not using titanium-stabilized, iron-chromium-molybdenum alloys in oxidizing solutions [*51*] applies to any solution in which the corrosion potential exceeds +0.1 V versus SCE.

The data of Table 8 show that sensitization in austenitic stainless steels associated with chromium carbide precipitates makes these alloys subject to intergranular attack over a wide range of corrosion potentials, −0.6 to 1.0 V versus SCE. This has been also demonstrated in potentiostatic tests [*57*]. Nevertheless, attempts have been made to use the potentiostat in short time tests to prove *immunity* to intergranular attack on sensitized Type 304 stainless steels at certain corrosion potentials [*58,59*]. In such potentiostatic tests, the potential of the specimen is held at the value which it is expected to have in the service environment. For example, using 1 N sulfuric acid at 90°C, the potential of sensitized Type 304 is adjusted to +0.6 V versus SCE. It is assumed that this would be its

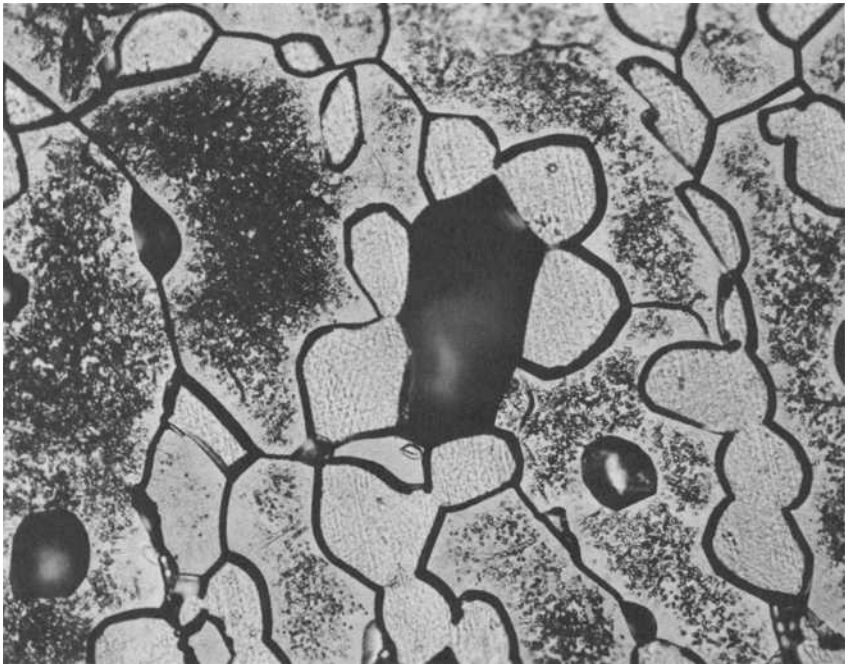

FIG. 34—*Initial attack in ferric sulfate test on sensitized Type 446 steel* [42] (×*500*). *Specimen: heated 1 h at 1150°C and exposed 14 h. Solution: boiling 50 percent sulfuric acid with 25 g/600 ml ferric sulfate. Structure: intergranular attack, but not on austenite-austenite boundaries.*

potential during exposure at 90°C to a plant solution of 1 N acid containing ferric sulfate. After holding for a relatively short time, less than an hour, the specimen was examined for evidence of intergranular attack. Because there was no intergranular attack during this brief test, it was assumed that sensitized steel could be used in this environment without danger of intergranular attack [*58*].

It has been shown [*60*] that this method is invalid. Such potentiostatic tests are actually simulated service tests at the same acid concentration, temperature, and corrosion potential as the service environment. There is no acceleration of the test conditions. Therefore, the length of time of the potentiostatic tests must be the same as that which would be needed to demonstrate immunity to intergranular attack on sensitized steel in an immersion test in the service environment. Such tests may require exposure periods of weeks or months. Actually, under potentiostatic conditions, only 30 h were required to reveal susceptibility in the test with 1 N acid at 90°C and a potential of +0.6 V versus SCE, as previously described. This was because the specimen had been sensitized in an unusually severe way by heating for 25 h at 677°C. The results of these lengthy potentiostatic tests have been confirmed by M. Henthorne [*11*].

From Table 8, it is also apparent that conclusions based on potential scans[11] must be limited to predicting behavior in solutions in which the specimen has a corrosion potential near that of the scan. For example, if a scan of a weldment of Type 446 stainless steel was made in sulfuric acid at a potential of −0.6 V versus SCE, it would be expected to show immunity to intergranular attack (Fig. 32). However, this conclusion is valid only for solutions having a similar oxidation reduction potential. It would not apply to corrosion in sulfuric acid with ferric sulfate in which the redox and corrosion potential is +0.6 V versus SCE and in which such a welded (sensitized) alloy is subject to intergranular attack (Fig. 34).

Finally, the electrode or corrosion potential of the stainless steel is not the only factor which determines whether or not there is intergranular attack on sensitized ferritic or *austenitic* stainless steels. The anion of the acid also affects this process. In boiling 10 percent hydrochloric acid, the corrosion potential of austenitic stainless steels is −0.4 V versus SCE, and there is no intergranular attack on sensitized specimens [*30,37*], even though this potential falls between that of the copper sulfate test with a potential of +0.1 V and the pure 5 percent sulfuric acid test with −0.6 V versus SCE. In both of these solutions, there is intergranular attack on sensitized (chromium carbide type) specimens (Table 8).

Effect of Sensitization on Stress-Corrosion Cracking, Pitting and Crevice Corrosion

The previous discussion has been confined to factors which cause susceptibility to intergranular attack in acids and to methods for detecting this susceptibility. During the past ten years, there have been service failures and laboratory studies which show that chromium carbide and molybdenum carbide precipitates are also associated with other forms of localized corrosion. Specifically, susceptibility to stress-corrosion cracking, pitting, and crevice corrosion has been related to the presence of these precipitates. To date, none of the intermetallic phases, precipitates, or products of equilibrium segregation, which cause preferential attack in oxidizing solutions, have been related to these other forms of corrosion.

Stress Corrosion Cracking

Ferritic stainless steels, such as Types 430 and 446, are generally considered to be immune to chloride stress-corrosion cracking. But welding

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[11] Vyas, B. and Isaacs, H. S., this publication, pp. 133-145.

impairs their ductility and their resistance to intergranular attack. In 1966, W. G. Renshaw [*61*] reported that welded Type 430 is subject to cracking in boiling solutions of sodium chloride containing only 50 ppm chloride. This phenomenon was then investigated by M. A. Streicher [*62*], who found that severely sensitized Type 446 also fails by stress corrosion in boiling water containing only 50-ppm chloride added as sodium chloride. Results on the relationship of sensitization to chloride stress corrosion cracking for various heats of 25Cr alloys are given in Table 9. Note that, when annealed (816°C) to replenish any chromium-depleted zones surrounding chromium carbide and nitride precipitates, the alloy is resistant not only in the dilute sodium chloride solution, but also in the much more severe 45 percent magnesium chloride (155°C) solution in a test of 100 days. This applies both to annealing after cold rolling and after a prior sensitizing heat treatment at 1204°C.

The effect of various sensitizing treatments on chloride stress-corrosion cracking depends on the severity of sensitization resulting from these treatments (Fig. 23). Ratios of ferric sulfate rates are listed in Table 9 as a measure of the severity of sensitization. Severe chromium depletion results in stress-corrosion cracking of the commercial heat of Type 446 steel in both chloride solutions. As might be expected on the sensitized (1204°C) specimen, cracking in the sodium chloride solution is completely intergranular (Fig. 35). However, in the magnesium chloride test, cracking is completely transgranular (Fig. 36). The crack path is confined entirely to ferrite grains, even though about 50 percent of the structure is made up of austenite grains because this commercial heat of Type 446 contains 0.2 percent nitrogen. Thus, it is not the crystal structure of the grains, face centered or body centered cubic, but their composition which determines susceptibility to chloride stress corrosion cracking. It has been frequently and erroneously assumed that the susceptibility of austenitic (18 percent chromium-8 percent nickel) stainless steels and the relative immunity of ferritic stainless steels are a function of their respective crystal structures.

To determine the relative importance of carbon and nitrogen in causing susceptibility to intergranular attack and to chloride stress corrosion, three separate laboratory alloys, one with 0.08 percent carbon, another with 0.2 percent nitrogen, and a third with very low carbon and nitrogen contents, were tested. Without carbon or nitrogen in the alloy, there is no effect of heat treatments on susceptibility to intergranular or stress corrosion (Table 9). Addition of 0.08 percent carbon produces a ferric sulfate ratio of 9.2 and makes the specimen subject to transgranular stress corrosion cracking in magnesium chloride solution, even though there was simultaneous intergranular attack in this solution which caused undermining and dislodgment of grains. Addition of more than twice as much nitrogen (0.2 percent) as carbon produces a ferric sulfate ratio of only 2.1.

TABLE 9—*Effect of heat treatment and composition on stress corrosion of Fe-25Cr alloys in boiling chloride solutions* [62].

					Stress Corrosion Cracking[c]	
Alloy	Heat	Heat Treatment or Deformation[a]	Microstructure	Ferric Sulfate Test, Ratio[b]	Magnesium Chloride 45%—155°C (transgranular)	Sodium Chloride 50 ppm Cl— 100°C (intergranular)
AISI 446	HD-8	cold rolled + annealed at 816°C, WQ	ferrite (small grains)	1.0	none[d]	none[d]
AISI 446	HD-8	1038°C, 1 h, WQ	ferrite	4.7	yes (<17 h)	none[d]
AISI 446	HD-8	1204°C, 1 h, WQ	ferrite and austenite	13.3	yes (17 h)	yes (617 h)
AISI 446	HD-8	1204°C, 1 h, WQ; plus 1 h at 816°C, WQ	ferrite plus chromium carbide and nitride ppt	1.4	none[d]	. . .
Fe-25Cr	R-2	1204°C, 1 h, WQ	ferrite	1.0	none[d]	none[d]
Fe-25Cr-0.08C	C-3	1149°C, 1 h, WQ	ferrite	9.2	yes (240 h)	. . .
Fe-25Cr-0.2N	C-4	1149°C, 1 h, WQ	ferrite and austenite	2.1	none[d]	. . .

[a] WQ = water quenched.

[b] Ratio of corrosion rates in 24-h ferric sulfate-50 percent sulfuric acid test.
Rate of heat-treated specimen divided by rate of mill-annealed (resistant) specimen.

[c] U-bend specimens. Time elapsed to appearance of first crack is shown in parentheses.

[d] No cracking after 2400 h of testing.

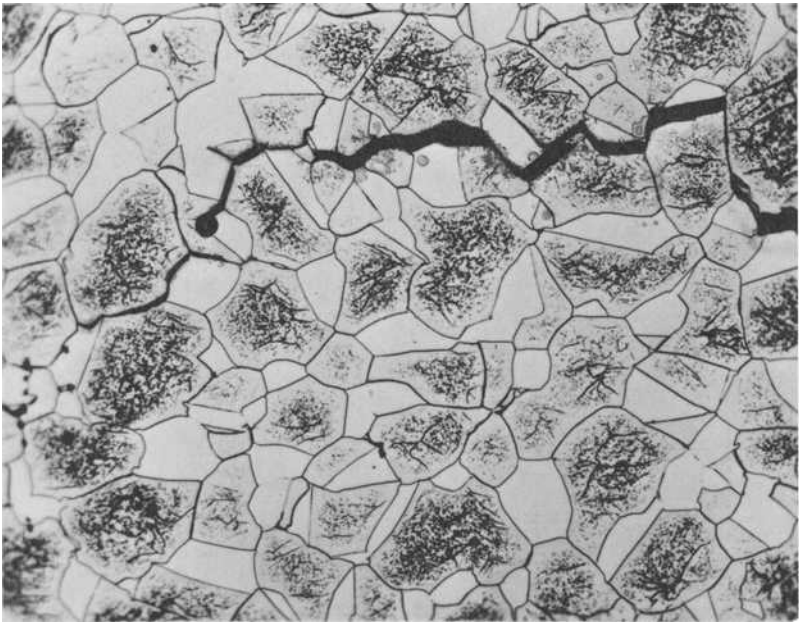

FIG. 35—*Stress-corrosion cracking of sensitized Type 446 steel in boiling sodium chloride solution* [62] (×*250*)*. Specimen: heated 1 h at 1200°C, water quenched, and formed into U-bend. Solution: boiling with 50-ppm chloride added as NaCl; 1610 h. Structure: intergranular cracking between austenite and ferrite grains. Etched electrolytically in oxalic acid.*

This degree of sensitization is not enough to make the alloy susceptible to stress corrosion in the tests of Table 9. On the basis of data in this table, a ferric sulfate ratio of 4.7 or greater is needed to make the 25Cr alloy susceptible to chloride cracking. The ratio concept appears to be a useful method for relating severity of sensitization to susceptibility to stress-corrosion cracking in the ferritic stainless steels in which chromium depletion rather than the presence of carbide and nitride precipitates makes the alloys subject to chloride stress-corrosion cracking.

It has also been found that susceptibility to intergranular attack associated with chromium carbide precipitates makes the new iron-chromium-molybdenum ferritic stainless susceptible to chloride stress-corrosion cracking. When the 29Cr-4Mo alloy contains carbon (210 ppm) in excess of the maximum amount specified, 100 ppm, it becomes subject to intergranular attack and to intergranular stress-corrosion cracking. Similarly, H. J. Dundas [*44*] (Footnote 8) has found that sensitized 18Cr-2Mo and 26Cr-1Mo alloys failed by stress corrosion in artificial seawater, and A. J. Sweet (Footnote 9) found that sensitized 26Cr-1Mo-Ti alloy fails in the wick test. In contrast, *austenitic* stainless steels are subject to *chloride* stress corrosion in the solution-annealed condition. Sensitization

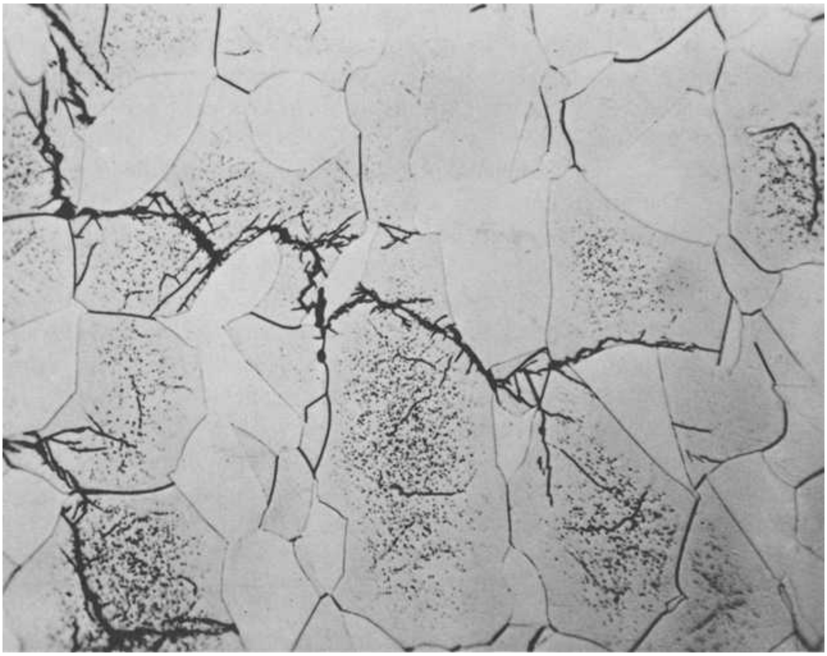

FIG. 36—*Stress-corrosion cracking of sensitized Type 446 steel in boiling 45 percent magnesium chloride solution* [62] *(×500). Specimen: heated 1 h at 1200°C, and formed into U-bend. Solution: 155°C, for 17.5 h. Structure: transgranular cracks in ferrite only. Etched electrolytically in oxalic acid.*

does not affect this process significantly. In both cases, the susceptibility is about the same, and the crack path is a mixture of trans- and intergranular. However, as already mentioned, in polythionic acid, cracking of austenitic stainless steels and also of Inconel Alloy 600 is a function of their susceptibility to intergranular attack. They are subject to cracking only when severely sensitized by chromium carbide precipitation [*39–41*].

Recently, it has been found in the nuclear power industry that sensitized austenitic stainless steels fail by stress-corrosion cracking in high-temperature water containing oxygen [*63,64*].[12] W. E. Berry et al [*63*] determined that there is intergranular stress-corrosion cracking in sensitized Types 304 and 316 in water at 288°C with 10-ppm oxygen. There was no cracking on solution-annealed Type 304. Also Types 304L and 347 steels were immune to cracking even after heat treatments that sensitize Type 304 steel but not these alloys. Thus, in this environment, only those alloys crack which have been made subject to intergranular attack.

Stress corrosion of Inconel Alloy 600 has been responsible for shutdowns of several nuclear plants. D. Van Rooyen [*65*] has recently summarized the

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[12] Taboada, A. and Frank, L., this publication, pp. 85–98.

findings in this difficult field. Intergranular stress-corrosion cracks have been found in a few heat exchangers exposed to high-temperature water. However, these intergranular cracks appeared only in solution-annealed material. There is evidence that sensitization actually *enhances* resistance to intergranular stress-corrosion cracking, perhaps because the chromium carbide precipitate dissolves elements (phosphorus, sulfur, silicon, nitrogen) segregated at the grain boundaries. It is these elements which are thought by some investigators to be the cause of the intergranular cracking rather than the carbide.

Beneficial effects of sensitization in Alloy 600 have also been reported by G. J. Theus [*66*]. He found that the most severely attacked material in an acid (ferric sulfate) test is the most resistant material in stress corrosion tests in 10 percent sodium hydroxide solution at 289°C.

In the solution-annealed condition, Hastelloy Alloys C and C-276 are among the most resistant alloys to intergranular attack, chloride pitting, and stress-corrosion cracking. As mentioned previously, certain thermal exposures may result in formation of a molybdenum-rich, M_6C carbide and an intermetallic precipitate. The carbide precipitate makes the alloy subject not only to intergranular attack in oxidizing and reducing acids, but also to stress corrosion cracking (Fig. 37) in magnesium chloride and ferric chloride solutions. Molybdenum-rich intermetallic mu-phase does not impair resistance to stress-corrosion cracking [*36*].

Pitting and Crevice Corrosion

Resistance to crevice and pitting corrosion of the highly resistant Alloy C is reduced when this material is sensitized. An alloy with 0.05 percent carbon is severely attacked in 10 percent ferric chloride solution at 50°C [*36*], even in cases of relatively mild sensitization with a ferric sulfate test ratio of only 2.0. Mu-phase does not have this effect.

One of the important properties of the new iron-chromium-molybdenum alloys is their resistance to chloride pitting and crevice corrosion. To obtain optimum resistance to chlorides, these alloys must be free of chromium carbide or nitride precipitates. When the carbon and nitrogen contents of the 29Cr-4Mo alloy are within the specified limits, the alloy resists sensitization and resists pitting and crevice corrosion in the two tests listed in Table 10. However, sensitization resulting from exceeding the concentration limits for carbon and nitrogen in the high-purity alloys (Table 6) or from incomplete stabilization in alloys containing titanium greatly impairs resistance to pitting and crevice corrosion.

Pitting tests were made on the two off-grade 29Cr-4Mo alloys whose response to sensitization is plotted in Fig. 24. Sensitization, either of the severe chromium carbide type (Fig. 24) or of the much less severe chromium nitride type, results in a loss of pitting resistance in the ferric

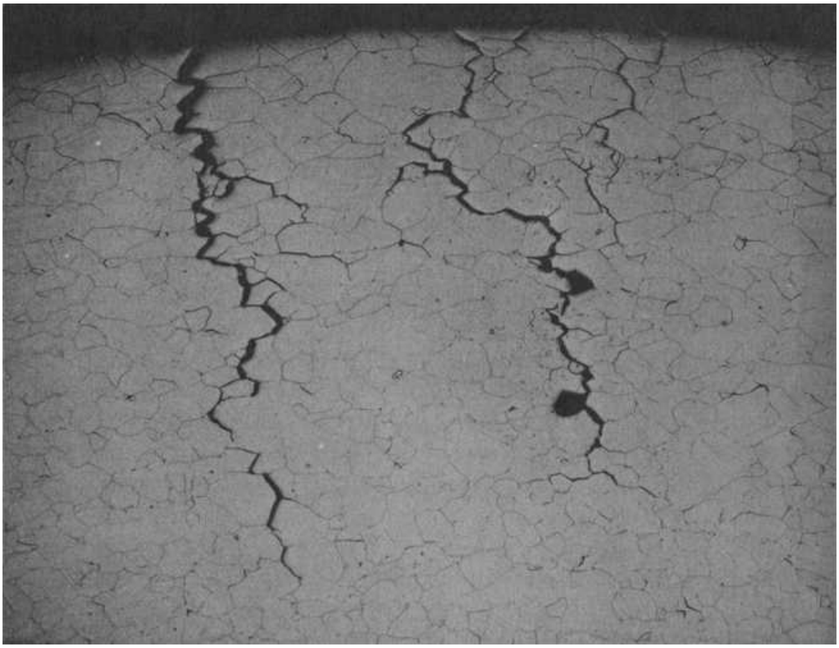

FIG. 37—*Stress-corrosion cracking in sensitized Alloy C-276* [36] (× *50*). *Specimen: 0.008 percent carbon, heated 1 h at 871°C (1600°F), water quenched, and formed into U-bend. Solution: boiling 45 percent* $MgCl_2$ *(155°C). Specimen exposed 2252 h.*

chloride test. The high-carbon heat is corroded in this test even in the solution-annealed condition. This may be a result of the impairment of passivity by carbon in solid solution previously observed in austenitic stainless steels [*67*]. The loss in pitting resistance of the relatively mildly

TABLE 10—*Effect of sensitization on pitting resistance of 29Cr-4Mo alloys. Effect of carbon and nitrogen.*

	Pitting Corrosion			
	2% $KMnO_4$-2% NaCl at 90°C		10% Ferric Chloride with Crevices at 50°C	
Alloy	Annealed	Sensitized	Annealed	Sensitized
Q-742 C—120 ppm N—645 ppm	no	yes	no	yes
Q-738 C—430 ppm N— 40 ppm	no	no	yes	yes

sensitized, high-nitrogen heat appears to be related to galvanic effects of the chromium nitride in this solution. In contrast, the much more severely sensitized high-carbon heat is not impaired in the less severe of the two tests. From extensive studies, it is known that the permanganate-chloride solution at 90°C is a less severe pitting medium than the 10 percent ferric chloride solution at 50°C [*52*]. A loss of pitting resistance because of sensitization has been also observed [*68,69*] in the 26Cr-1Mo alloy exposed in ferric chloride solution and in the 18Cr-2Mo-Ti alloy [*70*].

These examples extend the range of applicability of results obtained from evaluation tests for susceptibility to intergranular attack. To avoid susceptibility to chloride stress-corrosion cracking and to chloride pitting and crevice attack in certain environments, stainless steels must be resistant to intergranular corrosion in the evaluation tests. Conversely, these tests may be used to establish a certain degree of susceptibility in alloys to be exposed in a few specific environments in which the presence of chromium carbide precipitate has a beneficial effect.

When to Evaluate for Susceptibility to Intergranular Attack

All the stainless steels and nickel-rich alloys to which the various evaluation tests are applied (Tables 1 and 6) are relatively expensive. For example, in the form of 25.4-mm (1-in.) outside diameter welded tubing, the cost of Type 304 is three times that of carbon steel tubing. For Carpenter 20 Cb-3, this ratio is 13 times, and, for Hastelloy Alloy C-276, it is 27 times the cost of carbon steel. (These ratios are based on prices current in the spring of 1977.) However, for critical applications in the process and power industries, the replacement cost of the alloys is often only a relatively small part of the total cost of corrosion failures. The loss in production due to plant shutdowns can greatly exceed the costs of new equipment. For such critical applications, it is essential that the alloys be in their optimum metallurgical condition for resisting intergranular attack and other forms of corrosion associated with precipitates at grain boundaries.

Sensitized alloys, that is, materials containing potentially damaging precipitates at grain boundaries, may come into use on plants *inadvertently* when:

1. Regular carbon Types 304 or 316 are used unknowingly in place of Types 304L and 316L for fabrication involving welding.

2. The final mill annealing heat treatments and quenching operations are not effective on regular carbon grades of Types 304, Inconel Alloy 600, etc., in dissolving chromium carbides and nitrides and intermetallic phases and keeping them in solution during cooling.

3. There is incomplete stabilization of titanium- or niobium-bearing alloys (Types 321, 347, Alloys 625, 825, 18Cr-2Mo-Ti, and 26Cr-1Mo-Ti)

either because of inadequate amounts of these elements or because of ineffective stabilizing heat treatments.

4. Heat is applied for unscheduled forming operations during fabrication or installation of equipment.

5. The carbon or nitrogen contents or both of extra low-carbon austenitic stainless steels, the new high-purity iron-chromium-molybdenum alloys or Hastelloy Alloy C-276 exceeds the specified limits.

In some cases, sensitized material is used *knowingly* to reduce costs or, in a few cases, *intentionally* to minimize failures by stress corrosion in certain environments. When it is thought that there will be no intergranular attack by the process stream, sensitized material in the form of welded Type 304 or 316 may be used knowingly because such use can reduce costs in two ways. The regular carbon grades cost less than the extra low-carbon grades and have somewhat higher yield strengths which permit the design of smaller sections. Sensitization of these regular grades may also result from forming operations during fabrication and installation, or even as a result of final heat treatment of mill forms which may be carried out at temperatures known to cause sensitization, but which increase the strength, for example, of Alloy 600. As mentioned before, on Inconel Alloy 600, it has been found that sensitization reduces susceptibility to stress-corrosion cracking in some high-temperature water [*65*] and caustic [*66*] environments. Even in such cases, evaluation tests are needed to ascertain whether or not the required severity of sensitization has been achieved by the heat treatments used for this purpose.

When available plant experience shows that there will be intergranular or other localized attack on sensitized material, the alloy intended for such service must obviously be free of damaging grain-boundary precipitates and should, therefore, be resistant to intergranular attack in an appropriate evaluation test. However, when available data from plant service or long-time plant tests clearly show that a certain plant environment does not cause intergranular attack on sensitized alloys and when it is known that the process conditions will not change, there is no need to specify an evaluation test, or even to specify costly low-carbon grades. An example is a process in which stainless steels are used to prevent product contamination by corrosion products. In such cases, even carbon steel may have the necessary corrosion resistance from an engineering standpoint, but the corrosion products formed by the small amount of corrosion of carbon steel are not acceptable, and for this reason a stainless steel is used. Another example is the use of stainless steel for appearance or ease of maintenance.

This leaves new environments for which there are no actual or even comparable data on their effects on sensitized alloys. Even when a new environment is thought to be harmless, evaluation tests should, nevertheless, be applied to assure optimum metallurgical conditions. There have been a number of costly corrosion failures on sensitized material caused by previously unknown factors, such as oxygen in water at elevated temperatures (Footnote 12). Finally, even when the original environment is known not to cause intergranular attack on sensitized alloys, there may later be changes in process conditions which cause intergranular attack.

From this, it follows that, for critical service, sensitized alloys can be used only in those environments for which long-time service experience or plant tests have demonstrated immunity to attack on similarly sensitized material. Because service life may range from 10 to 40 years, the degree of sensitization which can be tolerated can be decisive. Therefore, the knowledge that sensitized material has been found to be free of intergranular attack for five to ten years in plant service can be used as a guide for future action only when there is information on the severity and type, carbide or sigma, of sensitization involved and on the effect of time on the rate of intergranular attack over the length of the expected service life. The degree of sensitization in the new equipment for the same environment should not exceed that of the material in service. Therefore, even in a case of the use of sensitized alloys for a critical application, evaluation tests are needed to determine the degree of sensitization in the form of a corrosion rate or a ratio of rate of the sensitized to rate of an annealed specimen.

Problems and Opportunities

The need for standardized test methods to detect susceptibility to intergranular attack in stainless steels and related alloys for quality control, alloy development, and research continues even though more than 50 years have elapsed since such tests were first applied to stainless steels. The need for these tests is greater today than in the recent past because of the introduction of new alloys and new production methods and the recognition that susceptibility to intergranular attack in acids may also affect other forms of localized corrosion, such as stress-corrosion cracking and pitting resistance. Another new factor is the use of the austenitic stainless steels and certain nickel-base alloys in critical environments to which they had not been exposed previously.

The melting and refining of new iron-chromium-molybdenum stainless steels in vacuum induction equipment and the use of consumable arc remelting of certain nickel-base alloys, for example, Hastelloy Alloy C-276, have made it possible to reduce carbon and nitrogen to very low concentrations. For stainless steels and nickel-base alloys with a somewhat higher tolerance for carbon and nitrogen, transfer of molten metal from electric arc furnaces to AOD vessels has provided effective means for reducing carbon, for controlling the concentrations of alloying elements, and for reducing costs. Introduction of continuous casting machines has also reduced production costs.

However, these new processes and changes have brought with them the potential for new problems. In high-purity alloys, close control of critical levels of carbon and nitrogen must be maintained. In stabilized alloys, the extent of combination of titanium with carbon and nitrogen must be monitored. Argon-oxygen refining causes greater erosion of the brick linings of AOD vessels than is the case in the arc melting process. As a result, the inclusion content of alloys made by the AOD process *may* be higher than that of alloys made by arc melting alone. Weldability has also been a problem on some heats made by the AOD process. Continuous casting can impair uniformity. Nevertheless, with optimum control of melting and casting variables and of welding techniques, AOD heats can have both lower inclusion contents and better weldability than heats made by arc melting only.

Incomplete exclusion of air from weld metals by shielding gases during welding of iron-chromium-molybdenum tubes can result in pickup of nitrogen by the molten weld bead. Carburization of low-carbon alloys by decomposition products from lubricants in contact with alloy surfaces can greatly increase their carbon content and decrease the corrosion resistance. Particularly for nickel-base alloys, variations in the thermomechanical history can greatly affect metallurgical properties and, therefore, the response to sensitizing conditions and corrosion resistance. Finally, before shipment, all mill forms require carefully controlled heat treatments to assure optimum properties. Such heat treatments, including solution annealing and heating to combine carbon and nitrogen with titanium in stabilized steels, may be carried out in protective atmospheres whose composition must be carefully controlled. ASTM standard test methods for detecting susceptibility to intergranular attack can continue to serve as important tools both for producers and users to assure optimum properties for safe and economical use of stainless steels and related alloys in critical, industrial applications.

To meet these rapidly changing needs, continuing improvements and simplifications in existing test practices are required. Ideally, these evaluation tests should provide clear-cut guidance for the nonspecialist, not only in the details of test procedures, but also in the selection of test methods and the application of criteria for assessing test results. Inadequacies in these categories can lead to erroneous results and misuse and misinterpretation of data derived from the tests. The following proposals are offered as "Indicated Activities" in continuation of those listed by F. L. La Que [*8*] in his summary of the 1949 ASTM symposium. They are based on the assumption that ASTM tests are intended to provide specific information by the simplest and most reliable procedures. In the early stages of development in this field, the available data were and still are diverse and limited. Because of this, several methods were established which provide the same information. Currently available data indicate that a number of improvements and simplifications in test practices are now possible. The following proposals are made to facilitate the development toward fewer, simpler, more reliable, and useful test practices.

Indicated Activities

1. *Remove the nitric acid test from A 262 and establish it as a separate ASTM test.* At present, the boiling 65 percent nitric acid test (Practice C) is specified for materials to be used in nitric acid service. Only this test is sensitive to sigma-phase in molybdenum-bearing austenitic stainless steels (Table 2). Also, problems such as end-grain corrosion associated with hexavalent chromium derived from corrosion products are unique to this solution. While this test also detects susceptibility to intergranular attack associated with chromium carbide precipitates, there are other tests which perform this function in less time and more simply. Furthermore, other test methods are actually more sensitive than the nitric acid test in detecting susceptibility to intergranular attack in Types 430 and 446 stainless steels (Figs. 22,23).

Thus, the nitric acid test should be used primarily as a *simulated service* test for alloys to be used in nitric acid environments. This is a return to its original function as defined by W. R. Huey [*4*]. When used in this way, it will be essential to specify the test apparatus, including the condenser, the ratio of surface area of test specimens to solution volume, and the number of changes of solution to provide a close simulation of the severity of the hexavalent chromium problem which the material being tested is to encounter in plant service. In A 262, Practice C, a wide-mouth Erlenmeyer Flask with a cold finger condenser (Fig. 7) is recommended for the nitric acid test.

It has been shown by J. E. Truman [*15*] that this condenser results in lower corrosion rates than the Allihn condenser. He made tests to examine whether the higher corrosion rates under Allihn condensers were attributable to access of oxygen or to the escape of some gaseous product and found that differences in rates between the two systems were related to the rate of removal of a gaseous reducing agent, an oxide of nitrogen, which kept the concentration of hexavalent chromium down. Thus, in his experiments, the cold finger condenser was more effective in keeping gaseous products in solution than the open Allihn condenser. This is in contrast to the situation with the copper sulfate test described previously in which the cold finger admits more air (oxygen) into the solution than the open Allihn condenser. These results indicate that additional research is needed to define the conditions for the simulated service tests in boiling 65 percent nitric acid.

It may be necessary to recommend more than one apparatus and procedure to simulate different nitric acid plant service conditions.

2. *Remove the nitric-hydrofluoric acid test* (*Practice D*) *from A 262.* This test is applicable only to Types 316, 316L, 317, and 317L stainless steels and has the advantage of detecting the type of susceptibility associated only with chromium carbides and not that associated with sigma-phase. Both the ferric sulfate (Practice B) and the copper sulfate (Practice E) tests provide the same results on these alloys. The nitric-hydrofluoric test is seldom used because of the special polyvinyl chloride apparatus required to handle hydrofluoric acid, the need for a carefully controlled water bath to maintain the 70°C test temperature, the care required to prevent loss of hydrofluoric acid vapors from the test solution which can result in low corrosion rates, and the hazards of handling hydrofluoric acid in the liquid and vapor states. Its only advantage is the short testing time of 4 h required, as compared with the 24 h for the copper sulfate and the 120 h for the ferric sulfate test. Even this advantage applies only to those specimens that do not pass the oxalic acid screening test (Practice A), which is applicable for use with the nitric-hydrofluoric acid test. Removal from A 262 does, of course, not prevent use of these well-established and authenticated procedures and evaluation criteria [22] for research or some other purposes. It merely simplifies A 262 by reducing unnecessary detail and duplication.

3. *Reduce the number of copper sulfate tests.*

(*a*) Current ASTM standards now contain two 16 percent sulfuric acid versions of the copper sulfate test, A 708 without metallic copper and Practice E in A 262 with metallic copper. A third version with 50 percent sulfuric acid and metallic copper is to be included in the new standard for ferritic stainless steels (Tables 7 and 11). In addition, the new standard will also include another description of the 16 percent sulfuric acid version with metallic copper. Therefore, the *Book of ASTM Standards* will then contain four descriptions of three different copper sulfate tests for evaluation of stainless steels.

Practice A 708 is a reintroduction of A 393 which was removed from the *Book of ASTM Standards* some years ago because it has been shown to detect only the most severe cases of sensitization. It was reinserted because an insensitive test was desired. Even as an insensitive test, it is ambiguous because the apparatus specified is "a suitable glass container." Data described previously, Table 4, show that the type of condenser can make a large difference in the rate of intergranular attack.

Rather than use an insensitive test for detecting only severe cases of sensitization by examination of a bent specimen for fissures, it appears safer and more informative to use one of the more sensitive tests, such as the 50 percent sulfuric acid tests with ferric or cupric sulfate. These tests would provide a quantitative (weight loss) measure of the degree of sensitization. By selecting a high acceptance rate or corrosion rate ratio, the

TABLE 11—*Copper sulfate tests.*

ASTM Designation	Solution: $CuSO_4$	Solution: H_2SO_4 (by weight)	Solution: Metallic Copper: Type	Solution: Metallic Copper: Contact	Apparatus	Evaluation	Testing Time (h)	Alloys
A 262-E	6%	16%	shot or turnings[a]	yes	Allihn condenser, 1-litre flask	bend test	24	austenitic stainless steel
A 708	6%	16%	none	. . .	suitable glass container	bend test	72	austenitic stainless steel
None (in preparation)								Fe-Cr with more than 25% Cr
Practice (Y)	72 g $CuSO_4 \cdot 5H_2O$ in 600 mil	50%	specimen	no	Allihn condenser, 1-litre flask	weight loss, bend test, no grain dropping	120	Type 446 (96 h) Fe-26Cr-1Mo Fe-26Cr-1Mo-Ti 29Cr-4Mo 29Cr-4Mo-2Ni
Practice (Z)	6%	16%	shot or turnings[a]	yes	Allihn condenser, 1-litre flask	bend test	24	Fe-Cr with 16 to 20% Cr 430 (17Cr) 434 (17Cr-1Mo) 436 (17Cr-1Mo-Nb) 18 Cr-Ti 18 Cr-2Mo-Ti

[a] Amount not specified; enough to cover the specimen.

desired degree of sensitivity could be specified. Thus, the objectives of A 708 can be realized more effectively with other tests, and this test could be removed from the *Book of ASTM Standards.*

(*b*) At present, the copper sulfate test with 50 percent sulfuric acid and metallic copper will be specified only for ferritic alloys and only for those containing 25 percent or more chromium (Table 11). However, tests on Type 430 (Fig. 22) and on Type 321 [*30*] steels indicate that it is also applicable to ferritic and austenitic stainless steels with only 18 percent chromium. Thus, there is a possibility that the test with 50 percent acid could serve for all alloys for which tests in copper sulfate solution are desired. Use of this test would provide the possibility of three methods of assessing test results, depending on the chromium and molybdenum content of the alloys. These are weight loss determinations and microscopic examination of bends for fissures or of flat specimens for dropped grains.

If future experiments verify these indications, the 16 percent acid test could then be removed from the new practice for ferritic alloys, and Practice E in A 262 could be replaced with the 50 percent acid test. The result would be that the same copper sulfate-50 percent sulfuric acid test would be included in both A 262 and the new practice for ferritic alloys.

Additional round-robin tests to relate oxalic acid etch structures on various alloys to performance in the 50 percent sulfuric acid-copper sulfate test are needed, as well as investigations of the optimum size of the copper specimen to be immersed simultaneously, but not in contact with the test specimen, and of the effect of corrosion products. Data in Figs. 10 and 15 show that, with the Allihn condenser, there is no need to put the stainless steel specimen into contact with the copper. Therefore, there is no need for a relatively large quantity of copper shot or turnings. With the Allihn condenser, simultaneous immersion of a copper specimen reduces the corrosion potential of the stainless steel to that of the copper specimen.

4. *Include assessment criteria in all test practices.* An important difference between the various evaluation tests in A 262, G 28, and the new standard for ferritic alloys is that some include criteria for assessment of the results and others do not (Table 5). The practice for the nitric-hydrofluoric acid test (A 262, Practice D) contains a paragraph (27.3) on the "significance of corrosion rate ratios," which states that "a value of 1.5 or less for the above ratios indicates that the degree of intergranular attack in the 10% HNO_3-3% HF acid test is not significant. A ratio of greater than 1.5 indicates that significant intergranular corrosion has occurred ... ." Similarly, in the copper sulfate test, Practice E of A 262, under Section "37, Evaluation," it is stated that "the appearance of fissures or cracks indicates the presence of intergranular attack." Photographs are provided of specimens bent after testing which illustrate resistant and fissured specimens. Similar criteria are given for the insensitive copper sulfate test of Practice A 708, but without the photographs.

The oxalic acid etch test, A 262, Practice A, also contains assessment criteria in the form of photomicrographs which are used to separate materials resistant to intergranular attack from those which have some susceptibility to attack and, therefore, must be tested in hot acid tests to determine the degree of susceptibility.

In contrast, in the nitric acid and the ferric sulfate tests in A 262, the user is merely shown how to convert weight loss measurements to corrosion rates without any guidance for assessing these rates. This is also the case in G 28 for the use of the ferric sulfate test on the eight types of nickel-rich alloys.

The new standard now in preparation for ferritic alloys provides for weight loss determinations, microscopic examination for dropped grains and examination for fissures on bent specimens (Table 7), depending on the test practice and the alloy being tested. Again, for the bend test, it is stated that "the appearance of fissures or cracks indicates the presence of intergranular attack," while, for the weight loss method, assessment is confined to "what corrosion rate is indicative of intergranular attack depends on the alloy and must be determined between the buyer and seller." For evaluation by microscopic examination, the only assistance provided is that "grain dropping is usually an indication of intergranular attack, but the number of dropped grains per unit area that can be tolerated is subject to agreement between the purchaser and seller."

To remove this inconsistency, assessment criteria should be included in the practices which now do not provide them. For each type of evaluation method, a criterion is needed which can be used to separate material resistant to intergranular attack from that which is clearly subject to a significant degree. This is now the case for the bends made on specimens exposed to the copper sulfate tests and corrosion rate ratios for the nitric-hydrofluoric acid test. For example, corrosion rates can be provided for each alloy for the nitric acid and the ferric sulfate tests which are indicative of the onset of significant susceptibility to intergranular attack. A list of such rates is given in Table 12 as a point of departure for consideration of this subject. Rates for additional grades of steel are needed for this list. Except for the rates given in parentheses, this criterion of a rate, which separates specimens which drop grains from those which do not, makes the sensitivity of the two tests of Table 12 equivalent to those of the nitric-hydrofluoric acid test with a ratio of rates of 1.5 and the appearance of fissures in the surfaces of specimens bent after testing in the copper sulfate test of Practice E.

Incorporation of such rates for each test practice still leaves the buyer and seller free to agree on some acceptance rate which meets their particular needs. The rates marked with a superscript *a* in Table 12 have proven useful as acceptance criteria for the du Pont Company and were derived from extensive experience in evaluation testing of a large number of specimens

TABLE 12—*Corrosion rates indicating susceptibility to intergranular attack. Corrosion rates higher than those listed indicate grain dropping in unwelded sheet specimens.*

Alloy (AISI Type)	Condition	Test Practice	Time, h	Corrosion Rate	
				mil/year	mm/year
304	as received	nitric acid, Practice C, A 262	240	12 (18)[a]	0.30 (0.45)
304L	20 min, 677°C	same	240	12[a]	0.30
304L	60 min, 677°C	same	240	12 (24)[a]	0.30 (0.60)
316	as received	same	240	12 (18)[a]	0.30 (0.45)
316L	20 min, 677°C	same	240	12	0.30
316L	60 min, 677°C	same	240	12 (24)	0.30 (0.60)
321	60 min, 677°C	same	240	24[a]	0.60
347	60 min, 677°C	same	240	24[a]	0.60
825	60 min, 677°C	same	240	36[a]	0.90
304	as received	ferric sulfate, Practice B, A 262	120	48[a]	1.20
304L	20 min, 677°C	same	120	48[a]	1.20
304L	60 min, 677°C	same	120	48[a]	1.20
316	as received	same	120	48[a]	1.20
316L	20 min, 677°C	same	120	48[a]	1.20
316L	60 min, 677°C	same	120	48[a]	1.20
317L	20 min, 677°C	same	120	48[a]	1.20
321	60 min, 677°C	same	120	36	0.90
430	as received	same	24	540	13.50
446	as received	same	72	120	3.00
Hastelloy Alloy C	as received	ferric sulfate, G 28	24	480	12.00
Alloy C-276	as received	same	24	360	8.00
Alloy G	as received	same	120	20	0.50
Carpenter 20Cb-3	as received	same	120	24[a]	0.60
Inconel Alloy 600	as received	same	24	24	0.60
Inconel Alloy 625	as received	same	120	18	0.45
Incoloy Alloy 800	as received	same	120	18	0.45
Incoloy Alloy 825	as received	same	120	18	0.45

[a] Used as acceptance rates by the du Pont de Nemours Co. When two rates are listed, the rate in parentheses is the acceptance rate.

and from laboratory investigations [*17,30,34-36,71*].[13] The only exceptions are the rates beside which a second rate is listed in parentheses in Table 12. The latter are the acceptance rates, while the lower rates beside them are indicative of the onset of grain dropping. The reasons for the rates in parentheses are described in the next section.

For the new standard on ferritic stainless steels (Table 7) the bend test is an available method for evaluation of the results for five of the tests listed. As described previously, this method provides a means for identifying specimens which are subject to intergranular attack as long as the tests are carried out for the length of time specified. Weight loss determination is listed as a possible method for evaluation in six instances. But the actual rates which separate resistant from susceptible material are available only for four of these: for Types 430 and 446 in the ferric sulfate test (Table 12) and for 26 percent chronium-1 percent molybdenum (120 h), 24 mil/year (0.6 mm/year) and for Type 446 in the copper sulfate-50 percent sulfuric acid test, 96 h, 120 mil/year or 3.0 mm/year.

In ten cases, microscopic examination for dropped grains is listed as a possible method for evaluation. In seven of these, it is the preferred method. Therefore, it is essential that the user be supplied with a criterion for assessing the surfaces after the test. Resistant material should be completely free of any undermined and dislodged grains on all parts of the test specimen. However, to avoid disagreements over the dislodgment of small grain fragments, a less severe criterion is desirable. In extensive series of tests, it was found that to be rated "resistant," a specimen, 2.5 by 5.0 cm, should not have more than three grains dislodged on either side. It is proposed that such a criterion, or a similar one, be included in the new practice as soon as possible.

Tests on stabilized iron-chromium-molybdenum alloys reported in this symposium (Footnotes 8,9) indicate that the oxalic acid screening test may be applicable to 18Cr-2Mo-Ti and 26Cr-1Mo-Ti alloys. More extensive surveys are needed.

5. *Devise a laboratory thermal treatment which simulates sensitization produced by welding.* This is the only important problem in F. L. La Que's [*8*] list of "Indicated Activities" of 1949 which has not been satisfactorily resolved. To assure immunity to sensitization during welding and stress-relieving treatments, certain heat treatments were selected about 40 years ago for application to specimens before testing. It was assumed that, if the specimens had "acceptable" corrosion rates after these heat treatments, they would not become sensitized by welding or by stress-relieving treatments. The first alloys developed to resist sensitization under these conditions were the titanium-stabilized, 18Cr-8Ni (Type 321) and the corresponding

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[13] Sweet, A. J., private communication, du Pont de Nemours and Company, Inc., Sept. 1977.

niobium-stabilized (Type 347) alloys. Also, because of the numerous particles of titanium or niobium carbides and nitrides in the structure of these alloys, they have higher general corrosion rates in the nitric acid test than the unstabilized 18Cr-8Ni (Type 304) alloy. These particles are dissolved in nitric acid, and the resulting pits concentrate hexavalent chromium ion corrosion product, which also increases the rate of attack independently of sensitization.

In studies of the effect of temperature on sensitization, it was found that, for the 18Cr-8Ni alloys, the temperature range is 430 to 870°C, with the temperature of most rapid formation of chromium carbide near 677°C (1250°F). Various thermal stress-relieving treatments fall into this sensitizing range. Therefore, to determine resistance to sensitization in stabilized alloys to be tested in the boiling nitric acid test, a widely used procedure was to heat specimens for 1 h at 677°C and water quench. To allow for the higher rates of general corrosion, the acceptance rates for these heat-treated stabilized alloys were increased from 0.45, the rate for solution-annealed Type 304, to 0.60 mm/year.

When the extra low-carbon versions of Types 304 and 316 alloys were introduced about 1948 in place of stabilized steels, they were also heated for 1 h at 677°C before testing. Even though they did not contain titanium or niobium carbides which increase the rate of general corrosion, the same acceptance criterion of 0.60 mm/year was applied to them. However, a specimen of Types 304L or 316L steel having this corrosion rate in the 240-h nitric acid test is subject to relatively severe intergranular attack. There is profuse grain dropping, "sugaring." In fact, the rate which divides susceptible from resistant material is only one half this rate, 0.30 mm/year. Nevertheless, this procedure has for many years successfully prevented failures by intergranular attack on welded or stress-relieved equipment; see rates in parentheses in Table 12. The reason for this is that the severe sensitizing heat treatment of 1 h at 677°C is compensated for by a generously high acceptance rate of 0.60 mm/year.

A large part of the specimens to be evaluated for critical applications consisted of Types 304L and 316L. The severe sensitizing heat treatments of 1 h at 677°C severely limited the percentage of specimens which could be screened by the oxalic acid test from the 240-h nitric acid or the 120-h ferric sulfate test. To increase the proportion which could be screened, it was proposed [*72*] that the heat treatment time be reduced to 20 min, and the acceptance rate reduced to 0.30 mm/year, the rate which divides material which drops grains from that which is resistant to intergranular attack. In a comparison of the two heat treatments and acceptance rates on duplicate specimens, it was shown that these are equivalent procedures but that the new procedure increases the proportion of sheet specimens which can be screened by the oxalic acid etch test from 25 to 65 percent [*72*].

The 20-min sensitizing treatment has been incorporated in A 262 as an optional method along with the 1-h treatment. Because the 20-min period is so short, a salt bath must be used for heating to shorten and standardize the time required to bring the specimen to the sensitizing temperature. For a 2.5 by 2.5 by 1.25-cm specimen, 12 min are required to bring it to 677°C in a furnace at temperature. This is reduced to 4 min in a salt bath [72].

Adoption of the 20-min sensitization procedure increases the proportion of specimens which can be screened by the oxalic acid etch test and provides an acceptance rate which corresponds to the beginning of grain dropping and is, therefore, essentially equivalent to all the other acceptance criteria, whether corrosion rates, the appearance of fissures in bent specimens, dropped grains, or the ratio of 1.5 for the nitric-hydrofluoric acid test. However, it still does not provide a heat treatment which simulates the thermal effects of welding. To date, the only way to obtain this is to make a weldment on test material of the same heat and thickness by the welding method to be used for fabrication. A specimen containing all components of the weldment is then cut out from this welded material for evaluation testing. Assuming that such test weldments can be made reproducibly to represent field practice, the problem then is to establish criteria for evaluating these specimens after testing. This is discussed in the next section.

The first use of a laboratory heat treatment for ferritic stainless steels which simulates the thermal effects of welding on susceptibility to intergranular attack has recently been described by H. J. Dundas and A. P. Bond (Footnote 8). In their paper, which is included in this publication, they show that on two of the new ferritic stainless steels, 18 percent chromium-2 percent molybdenum and 26 percent chromium-1 percent molybdenum, heating a small specimen for 5 min at 1205°C in an atmosphere of helium and then slow cooling gives corrosion test results which parallel those obtained on welded specimens of various heats of these two alloys. These results suggest that, for the ferritic stainless steels, it may be possible to devise a standard procedure for treating specimens before evaluation testing and thereby avoid the need for testing welded specimens. For standardization, the specimen size, heating procedures, and cooling rates need to be determined for the sensitizing procedures.

6. *Establish criteria for evaluation of weldments.* The various components of weldments are shown in Fig. 38, which is based on the classification scheme of W. F. Savage [*73*]. The weld nugget or the composite region contains the bulk of filler metal which is somewhat diluted with material melted from surrounding base metal. Adjacent to the nugget is a zone of base metal which melted and solidified during welding without experiencing mechanical mixing with the filler metal, the unmixed zone. In these two regions, there is complete melting, resulting in a cast structure. Beyond this weld interface, there is a partially melted zone within which the proportion melted ranges from 100 to 0 percent. The heat-affected zone is that portion of the base metal within which all microstructural changes produced

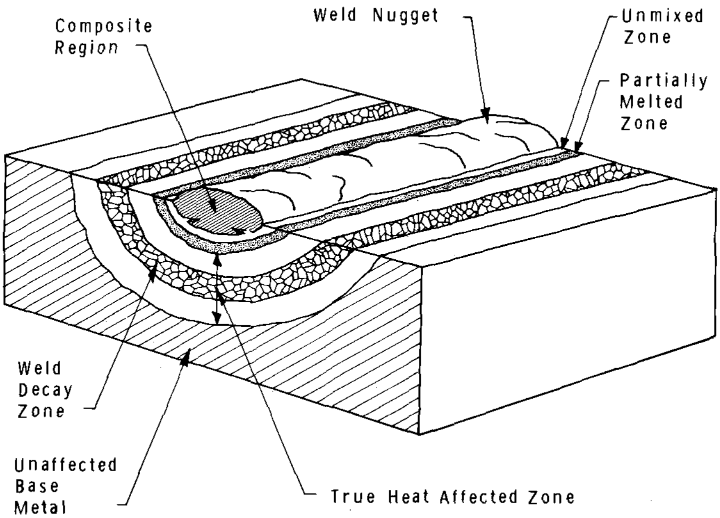

FIG. 38—*Schematic diagram of components of weldment in austenitic stainless steel. Diagram is based on findings of W. F. Savage* [73].

by welding occur in the solid state. The maximum temperature reached in the heat-affected zone is highest near the molten zone and decreases with distance from this interface.

Note that the weld decay zone which contains chromium carbide precipitate is not adjacent to the cast metal, but at some distance from it, in austenitic stainless steels. The reason for this is that the temperature of the metal in the zone adjacent to the molten zones has been raised above the chromium carbide precipitation range. During cooling, the precipitation range is traversed from above. It has been shown [*36*] that carbide precipitation is much slower when the sensitizing range is entered from above. Thus, both because of this factor and because the total time in the precipitation range is relatively short, there is no carbide precipitate in the zone adjacent to the partially melted zone. In the weld decay zone (Figs. 38,39), the metal is heated into the carbide precipitation range, and the time in this range is longer than that of the zone adjacent to the partially melted zone [*74*]. Beyond the weld decay zone, the temperature remains below the sensitizing range during the welding operation.

In effectively stabilized austenitic stainless steels (Types 321 and 347), there is no weld decay zone. However, immediately adjacent to the partially melted zone, the temperature is so high that the titanium or niobium carbides are dissolved in the solid solution before rapid cooling through the sensitizing range. As in the case of unstabilized steels, cooling from above the sensitizing range is rapid enough to keep the carbon in solid

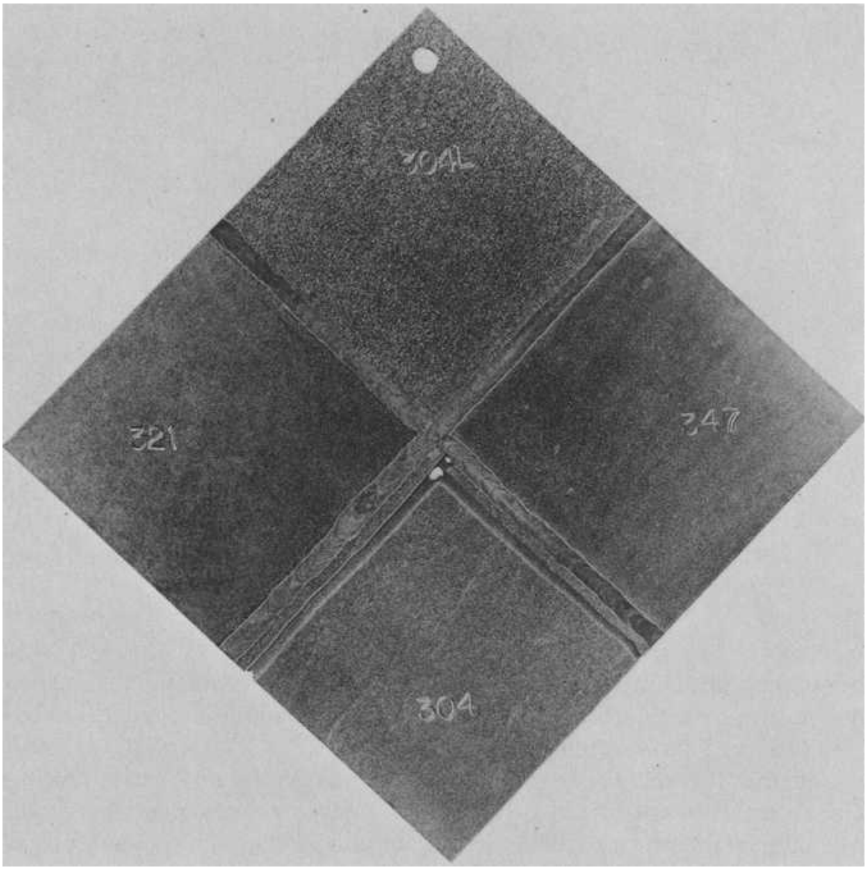

FIG. 39—*Weld decay and methods for its prevention. The four different panels were joined by welding and then exposed to a hot solution of nitric-hydrofluoric acids. The weld decay, such as shows in Type 304 steel, is prevented by reduction of the carbon content (Type 304L) or stabilization of carbon with titanium (Type 321) or niobium (Type 347).*

solution and is too rapid to form titanium or columbium carbides. However, when weldments in stabilized steels are later heated into the sensitizing range, for example, during a stress-relieving treatment or another weld pass, chromium carbides form, and this zone becomes sensitized. Exposure to certain acid solutions results in intergranular attack in a narrow zone next to the partially melted zone, knife-line corrosion [*75*]. It can be prevented by heating the weldment at 900°C to react the stabilizing element with carbon to form niobium or titanium carbides. As a result, there is no carbon available to form chromium carbides during subsequent exposure in the carbide precipitation range, 430 to 870°C.

Figure 30 illustrates intergranular attack on an autogeneous weldment (made with tungsten electrode without filler metal) in a 29Cr-4Mo alloy with a nitrogen content which greatly exceeds the maximum permissible concentration of 200 ppm. Intergranular attack takes place in the melted metal and in a narrow zone immediately adjacent to it. Apparently, the high temperatures in these zones resulted in the slowest rates of cooling through the sensitizing range (Fig. 24) and the precipitation of chromium carbides at grain boundaries.

When weldments are made to simulate fabrication welds or when they are part of the tube producing process, they then contain the very components which will be exposed in service, the same compositions, structures, and thermal cycles. Any evidence of intergranular attack in any of the components of the weldments will, therefore, be an indication of susceptibility during long time exposure in those service environments which are known to cause such attack on sensitized material. Because of this, assessment of weldments after exposure in laboratory evaluation tests must be based on very strict criteria for the onset of intergranular attack. Such criteria include the appearance of fissures on specimens bent after testing and evidence of dropped grains. Weight loss measurements are generally too insensitive to detect intergranular attack confined to narrow zones of a weldment. To implement this method of assessing corrosion on weldments, tests are needed in nitric, ferric sulfate, and cupric sulfate solutions on weldments prepared by the various methods applicable to each alloy for which the new assessment criteria are to be established. In addition, where applicable, the results should be compared with the oxalic acid etch structure of the weldment on cross sections perpendicular to the weld bead.

In some cases, there is preferential attack on weld filler metal in austenitic stainless steels related to its ferrite content. R. W. Gurry et al [*76*] have found that chloride-containing acids, strong organic acids, and sulfuric acid preferentially attack weld metal containing more than about 5 percent ferrite, whereas the oxidizing acids, nitric and ferric sulfate-sulfuric acid, used in evaluation tests do not cause preferential attack on ferrite-bearing weldments. Removal of the ferrite by cold working and annealing eliminates this form of preferential attack. Thus it may be possible to screen weldments for service in reducing acids by microscopic (oxalic acid etch) testing for the presence of ferrite. To establish a series of standard etch structures for evaluation, comparisons are needed between etch structures containing various amounts of ferrite and the corrosion in reducing acids of these same weldments.

7. *Evaluate castings on the basis of oxalic acid etch structures.* Castings generally have much larger grains than wrought materials. As a result, the time required to undermine and dislodge grains from sensitized specimens in the acid corrosion tests is much longer than in the case of small-grained, wrought materials. Therefore, the weight loss of castings tends to

be small even though there may be significant attack at grain boundaries. Only when the grains at the surface are undermined completely does the weight loss increase significantly. The time required for this may exceed the standard testing time *t* in Fig. 40.

In practice, castings rarely fail in hot acid evaluation tests, even though they may be severely sensitized. Examination for fissures on specimens bent after testing would reveal attack at boundaries, but cast specimens generally do not lend themselves to bending. Doubling and tripling the length of the standard test period may provide a more realistic corrosion rate.

Because of these problems, it is proposed that castings of austenitic stainless steels be evaluated entirely on the basis of their oxalic acid etch structures. Photographs of five pertinent etch structures have been incorporated in A 262, Practice A. The first three show typical step and ditch structures. The other two illustrate ferrite in a form which is resistant in oxidizing solutions in which the corrosion potentials range from +0.1 to 1.0 V versus SCE and a form in which it is not resistant in these solutions. It is proposed that the microstructures in Practice A of A 262 be used, not just for screening for hot acid corrosion tests, but to accept or reject castings for plant service without recourse to the hot acid test.

As described in Section 6, austenitic weld metal, also a cast structure, may contain some ferrite. It may be, therefore, subject to preferential attack in certain *reducing* acids. Oxalic acid etch structures containing ferrite (or amounts in excess of a defined limit) would be rated as unacceptable for such service. More data are needed on the types of reducing acid solutions in which ferrite in castings impairs corrosion resistance and on the amounts of ferrite which result in a significant increase in corrosion rates.

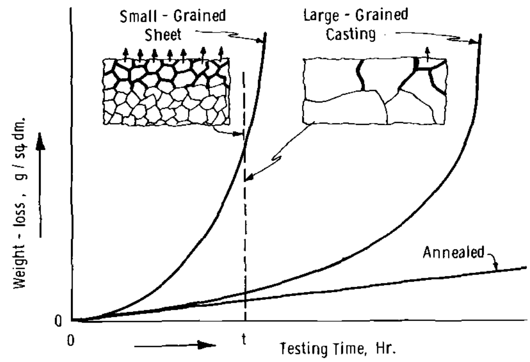

FIG. 40—*Schematic representation of the effect of grain size on intergranular corrosion. When intergranular corrosion is measured by weight loss, it may not be detected on large-grained materials, such as castings, during the test period* (t) *specified for wrought* (*smaller-grained*) *material. The time required to dislodge large grains is much longer than that for small grains.*

8. *Investigate the role of intermetallic phases in stainless steels and nickel-rich alloys.* As described earlier, the formation of intermetallic phases or equilibrium segregation of alloying elements (chromium, molybdenum at grain boundaries results in preferential attack on molybdenum-bearing austenitic stainless steels, for example, Type 316L in nitric acid. In 18Cr-2Mo-Ti and Fe-26Cr-1Mo-Ti alloys, intermetallic phases lead to preferential attack in both the nitric and ferric sulfate-sulfuric acid solutions. M. H. Brown and R. W. Kirchner [*77*] have reviewed available information on sensitization of wrought, high-nickel alloys. They concluded that submicroscopic phases also contributed to susceptibility to intergranular attack in molybdenum-bearing stabilized alloys, such as Inconel Alloy 625, Incoloy Alloy 825, and Carpenter 20 Cb-3. Investigations are needed to identify these phases, to characterize their resistance to various acids, and to determine their effects on other forms of localized corrosion, such as stress-corrosion cracking and pitting resistance. On the basis of the results, it should then be possible to correlate these properties with the performance of these alloys in evaluation tests.

In the case of Hastelloy Alloys C and C-276, this type of investigation has demonstrated [*36*] that the molybdenum-rich intermetallic compound, mu-phase, is without significant effect on corrosion in reducing acids and in chloride pitting and stress corrosion environments. Only in oxidizing acids is there impairment of the resistance to intergranular attack (Table 13). In contrast, the molybdenum-rich carbide impairs resistance to all of these forms of corrosion.

9. *Improve the standard (G 35) for testing in polythionic acid.* The polythionic acid test solution in ASTM Recommended Practice for Determining the Susceptibility of Stainless Steels and Related Nickel-Chromium-Iron Alloys to Stress Corrosion Cracking in Polythionic Acids (G 35-73) is made by first bubbling sulfur dioxide gas through a fritted glass bubbler submerged in a container of distilled water until the solution is saturated. Then hydrogen sulfide gas is slowly bubbled into the same solution. The simplest method for checking the solution for polythionic acids is to expose a stressed and sensitized specimen of Type 302 stainless steel. The specimen should fail by cracking in less than 1 h. R. L. Piehl [*78*] has concluded that it is probable that sulfurous acid actually is the primary agent that causes this type of cracking.

Additional investigations are needed to establish the agent which is the cause of cracking. If sulfurous acid is found to be the sole cause, this will simplify the preparation of test solutions and also make it possible to define its composition more precisely.

Because cracking is a function of the degree of sensitization, a precise measure of this degree should be a part of this test procedure. One of the quantitative acid corrosion tests, nitric, ferric sulfate-50 percent sulfuric acid, or copper sulfate-50 percent sulfuric acid with metallic copper, should

TABLE 13—*Summary of phases formed and their effect on localized corrosion of Ni-Cr-Mo alloys* [36].

	Type of Molybdenum-Rich Precipitates (1-h heat treatments)	
Alloy	M_6C	Mu-Phase
Alloy C	yes	yes
Alloy C-276	yes[a]	yes
Alloy C-4	no	yes[b]
Form of Corrosion		
intergranular[c]		
reducing acids (−0.6 V versus SCE)	yes[d]	no
oxidizing acids (+0.6 V versus SCE)	yes	yes
chloride crevice attack	yes	no
chloride stress corrosion cracking	yes	no

[a] No, when carbon is 0.004 percent or less.

[b] Properties like those of mu-phase. The precipitate is rich in titanium.

[c] In the copper sulfate-50 percent sulfuric acid test (+0.1 V versus SCE), neither the carbide or Mu-phase precipitates have a significant effect on susceptibility to intergranular attack. Apparently the solution is not oxidizing enough for preferential attack on the molybdenum-rich precipitates.

[d] No, when carbide is formed at high temperature and there is extensive rediffusion of molybdenum-depleted zones.

be applied to a duplicate specimen for determining the degree of susceptibility to intergranular attack in the material to be tested for susceptibility to stress-corrosion cracking. Either a corrosion rate or a ratio of the corrosion rate of the sensitized to the rate of an annealed specimen should be determined.

At present, "any type of stress corrosion test specimen can be used with this test solution." No solution volumes or specimen sizes are specified or recommended. More guidance and better definition of test conditions are needed. Also, data are needed on the applicability of the test to specific alloys, including the new ferritic stainless steels.

If it is possible to relate severity of intergranular attack for a given alloy to susceptibility to cracking in polythionic (sulfurous) acids, it may be possible to do it without this stress-corrosion test. To avoid failures by cracking in polythionic acids, specify materials whose degree of sensitization is less than a specified limit.

10. *Determine the effect of surface preparation on the corrosion of nickel-base alloys.* In general, corrosion of nickel-base alloys is more strongly influenced by their thermomechanical history than is the case for austenitic stainless steels [77]. The effect of sensitizing heat treatments varies greatly with this history. Even surface grinding after sensitizing heat treatments or of as-received material in preparation for corrosion testing can have a major ef-

fect on the corrosion process, especially in the case of Inconel Alloy 600. The surface preparation of specimens needs to be defined carefully on the basis of new investigations of this problem. A thin layer of surface metal on ground specimens of sensitized Alloy 600 is sometimes completely resistant to intergranular attack. At points, such as edges, where the solution can avoid this layer, there may be rapid intergranular attack which undermines the unattacked surface layer.

Summary of Simplified Test Program

Stage One—If the various proposals made in the previous section for removal of test practices and changes in applicability of tests are implemented, the tests listed in Tables 5 and 7 would be transformed into the series shown in Table 14. All tests are to include assessment criteria for determining the presence of significant susceptibility to intergranular attack.

(*a*) Austenitic and ferritic stainless steels and nickel-rich alloys which are to be used in environments containing nitric acid are to be tested in the boiling 65 percent nitric acid test. The apparatus and procedures are to simulate plant conditions in their effect on the accumulation of corrosion products and gases evolved. Except on weldments, corrosion is to be determined by weight loss after 240 h of exposure. Weldments are to be evaluated by microscopic examination for evidence of grain dropping. This expanded version of the old Practice C of A 262 is to be described under a new ASTM designation.

(*b*) The current Practices in A 262 are to be confined to the oxalic acid etch test (Practice A), the ferric sulfate test (Practice B), and the copper sulfate test with 50 percent sulfuric acid, which is to replace the copper sulfate-16 percent sulfuric acid solution, Practice E. All three tests are for wrought austenitic stainless steels, with the oxalic acid etch test to serve, as now, to screen specimens in conjunction with the other two tests. In addition, the etch test is to be used as an acceptance-rejection test on austenitic stainless steel castings.

Weight loss measurements can be used to determine susceptibility to intergranular attack in both sulfuric acid tests. In the test with copper sulfate, the use of optical evaluations for dropped grains and fissures in bends may also be desirable. These two methods are also to be applied to the evaluation of weldments exposed to both sulfuric acid tests.

(*c*) The new practices for ferritic alloys in Table 7, which have not yet been incorporated in the *Book of ASTM Standards,* can be reduced to two by eliminating the copper sulfate test with 16 percent sulfuric acid. This is done by testing all of the alloys in the copper sulfate solution with 50 percent acid and varying the testing time with the chromium content. All three assessment methods can be applied on a selective basis. Weldments can be evaluated by optical criteria, grains dropped, and fissures in bends.

TABLE 14—*Summary of proposed test program: Stage I.*

Standard Practice[a]	Test Solution[b]	Methods of Evaluation[d]	Purpose and Applicability
New[f]	65% nitric acid	weight loss	simulated service test for alloys to be exposed in nitric acid environments; austenitic and ferritic stainless steels. Nickel-rich alloys.
A-262			
Practice A	oxalic acid etch	etch structures	screening test for ferric sulfate and copper sulfate tests on wrought austenitic stainless steels; acceptance-rejection test on austenitic castings.
Practice B	ferric sulfate-50% sulfuric acid	weight loss	acceptance testing of wrought, austenitic stainless steels
New practice	copper sulfate-50% sulfuric acid with metallic copper (Allihn condenser	weight loss, dropped grains, bend test	acceptance testing of wrought austenitic stainless steels
New[c] (ferritic alloys)[e] Practice *X*[f]	ferric sulfate-50% sulfuric acid	weight loss,[g] dropped grains, bend test	acceptance testing of ferritic stainless steels Type 430, 446 26Cr-1Mo 29Cr-4Mo 29Cr-4Mo-2Ni

Practice Y[f]	copper sulfate-50% sulfuric acid with metallic copper (Allihn condenser)	weight loss,[g] dropped grains, bend test	acceptance testing of ferritic stainless steels Types 430, 434, 436, 446 18Cr-Ti 18Cr-2Mo-Ti 26Cr-1Mo 26Cr-1Mo-Ti 29Cr-4Mo 29Cr-4Mo-2Ni
G-28 (Unchanged)	ferric sulfate-50% sulfuric acid	weight loss	acceptance testing of nickel-rich alloys Alloy 600, 625, 800, 825 Carpenter 20Cb-3 Hastelloy Alloys G, C, and C-276

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[a] The function of ASTM A 708 can be provided more effectively by tests in A 262 and it is, therefore, not a part of the proposed program.

[b] The nitric-hydrofluoric acid test is not included because other tests provide the same information. The copper sulfate-16 percent sulfuric acid test has been replaced by the more rapid and quantitative test with 50 percent acid.

[c] The copper sulfate-16 percent sulfuric acid test has been removed because the 50 percent acid test can provide the same information.

[d] Assessment criteria for noting the presence of significant susceptibility to intergranular attack are to be included in all test practices.

[e] It is assumed that stabilized alloys will not be used in highly oxidized acids.

[f] The oxalic acid etch test can be used to screen specimens on a selective basis.

[g] Weight loss criterion does not apply to 29Cr-4Mo and 29Cr-4Mo-2Ni alloys.

(*d*) Ferric sulfate tests in G 28 for nickel-rich alloys remain unchanged. Weight loss is used to determine corrosion rates. Welded specimens are evaluated by optical methods.

(*e*) ASTM G 35 is not listed in Table 14 because it should probably be removed from the *Book of ASTM Standards.* Its function can probably by filled by the two 50 percent sulfuric acid tests, with ferric or copper sulfate (A 262 in Table 14). The problem really is to prevent stress corrosion cracking in polythionic acid solutions, and this can be accomplished by using stainless steels whose degree of sensitization does not exceed a certain limit which can be detected by the two sulfuric acid tests.

Stage Two—A further stage of simplification of procedures and reduction of the number of test practices appears possible. Extensive comparisons of test results on duplicate specimens exposed to several evaluation tests will be required to realize the program of practices given in Table 15. However, current developments in the production of extra-low-carbon, austenitic stainless steels and the savings in testing costs and time appear to make its attainment possible and desirable.

(*a* The nitric acid test and ASTM G 28 retain their function as in Table 14.

(*b*) Increasingly larger percentages of Types 304L and 316L stainless steels are being made by argon-oxygen refining. There has been a progressive reduction of the carbon content of these alloys to about 0.02 percent.

By using the 20-min sensitizing treatment, it can be expected that an ever higher percentage of all such specimens subjected to evaluation testing has either a step or dual structure in the oxalic acid etch test. Therefore, it may be possible to use this etch test as an acceptance test without recourse to either the ferric or copper sulfate tests with 50 percent sulfuric acid. The few specimens having a ditch structure would be classed as unacceptable. Mill-annealed Types 304 and 316 also can be evaluated in this manner because they are not sensitized in the laboratory before testing. Evidence of susceptibility to intergranular attack (ditch structure) in such material is rare and should also lead to an unacceptable rating. For these reasons, both the ferric and copper sulfate tests have been removed from A 262 in Table 15.

(*c*) Limited available data indicate that the copper sulfate-50 percent sulfuric acid test can provide the same information as the ferric sulfate test on the alloys listed for Practice X in Table 14. If this point is supported by more extensive testing, all ferritic alloys can be evaluated in the copper sulfate test, and Practice X can be removed from the new standard for ferritic stainless steels.

Acknowledgment

It is a pleasure to acknowledge the skilled assistance of my long-time associate, S. J. Kucharsey, beginning with the work on the oxalic acid

TABLE 15—*Summary of proposed test program: Stage II.*

Standard Practice	Test Solution	Methods of Evaluation[a]	Purpose and Applicability[b]
New	65% nitric acid	weight loss	simulated service tests for alloys to be exposed in nitric acid environments
A262 Practice A	oxalic acid etch	etch structures	acceptance test for detecting susceptibility to intergranular attack in austenitic stainless steels, wrought and cast
New (ferritic alloys) Practice Y[c]	copper sulfate-50% sulfuric acid with metallic copper (Allihn condenser)	weight loss,[d] dropped grains, bend test	acceptance test for all ferritic stainless steels (17 to 30% Cr)
G 28	ferric sulfate-50% sulfuric acid	weight loss	acceptance test for nickel-rich alloys

[a] Assessment criteria for noting the presence of significant susceptibility to intergranular attack are to be included in all practices.

[b] For detailed lists of alloys for each practice, see Table 14.

[c] It is assumed that stabilized alloys will not be used in highly oxidized environments.

[d] Weight loss criterion does not apply to 29CR-4Mo and 29Cr-4Mo-2Ni alloys.

etch test and the ferric sulfate test and extending through the work on the role of copper in the copper sulfate test.

More recently, A. J. Sweet assisted with the tests on stress-corrosion cracking and R. L. Colicchio with the work on ferritic alloys and polythionic acid. The latter was a result of a problem brought to our attention by T. F. Degnan. C. G. Henderson took the photographs on the scanning electron microscope, and L. B. Eichelberger prepared the drawings.

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Intergranular Corrosion in Nuclear Systems

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ABSTRACT: The occurrences of intergranular stress-corrosion cracking in nuclear power plant components made of austenitic alloys are discussed. Cracks of this type have occurred in sensitized Types 304 and 316 austenitic stainless steels in a variety of components at various stages of fabrication. Historically, cracking in early reactors occurred in heavily sensitized material or were related to the presence of chlorides or caustic ions. More recently, a rash of cracks were found in boiling water reactor piping adjacent to welds. This problem is evaluated.

Wastage and intergranular cracking of Inconel 600 alloy tubing of steam generators has occurred in the secondary side in plants that have used either sodium phosphate or all volatile water treatment. Design and environmental factors have had a pronounced influence on the tube degradation. The significance of these conditions is discussed, as is action taken by the Nuclear Regulatory Commission relating to this problem.

KEY WORDS: austenitic stainless steels, nickel alloys, inter-granular stress corrosion cracking, nuclear reactor materials, pipes (tubes), sensitizing, welding, boiler tubes, water chemistry

The nuclear industry is no stranger to stress-corrosion cracking. Numerous alloys, including austenitic stainless steels and Inconel 600 (a high-nickel alloy), have failed in nuclear power systems commencing in the late 1950s when the nuclear industry was beginning. The problem has become progressively more common as more reactors and associated systems have been constructed. In recent years, significant delays and costs have resulted because of the need to repair or replace failed components.

Austenitic Stainless Steel

Austenitic stainless steels have been used extensively in the construction of nuclear reactor plants. The major components of the primary coolant

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systems in water-cooled reactors are constructed from these alloys, which are relatively inexpensive, have excellent mechanical properties, and are readily fabricated into large integral assemblies designed to have a high degree of structural integrity. Also, austenitic stainless steels have excellent corrosion resistance to reactor coolants; this is an important consideration since radiation levels in these systems are related to the amount and distribution of corrosion products.

Although uniquely suited for nuclear systems in many respects, austenitic stainless steels have one major drawback that has plagued the nuclear industry since its inception. These materials are susceptible to stress-corrosion cracking (both transgranular and intergranular varieties, depending on the circumstances) that may result in failure of the component affected.

In austenitic stainless steel, stress-corrosion cracking results from a combination of high tensile stresses and corrosive environments acting synergistically to penetrate the protective oxide and proceed through the material at a relatively rapid rate. For stainless steel, environments that cause stress-corrosion cracking include aqueous solutions of chlorides, fluorides, hydroxide ions, or dissolved oxygen. Very small amounts may lead to cracking, particularly if permitted to concentrate. These effects of chlorides and hydroxides are classic and have been well documented for many years, but stress-corrosion cracking due to fluorides or dissolved oxygen has been observed only comparatively recently. Susceptibility to stress-corrosion cracking is related to the level of tensile stresses, which may occur, for example, as primary loadings, residual stresses due to welding or fabrication, or thermally induced stresses. In engineering structures, such stresses are frequently difficult to control or predict, and high levels may exist in local regions, resulting in rapid failure. In nuclear systems, these steels have been particularly susceptible when in the "sensitized" condition.

Sensitization of Stainless Steel

Sensitization results from heating nonstabilized stainless steel such as Types 304 and 316 in the temperature range of about 427 to 871 °C (800 to 1600 °F), causing precipitation of chromium-rich carbides, essentially continuously, along grain boundaries. The regions alongside these grain boundaries are much more susceptible to attack than the remainder of the material, and, when stainless steel in this condition is exposed to certain environments, its susceptibility to intergranular attack is greatly increased. In this condition, the material is considered sensitized. Sensitization may result from heat treatment, welding, slow cooling through the sensitizing temperature range, or operating at these temperatures. Common methods of controlling sensitization include (*a*) heat treating above approximately 982 °C (1800 °F) to put carbides in solution, (*b*) reducing the carbon content of the steel, (*c*) adding stabilizing elements to tie up the carbide preferentially, and (*d*) modifying the analysis of the material to produce a duplex structure of ferrite in an austenite matrix (at least 5 percent ferrite), such as generally occurs in austenitic stainless steel weld metal and castings.

Early Occurrences of Stress-Corrosion Cracking

Stress-corrosion cracking has occurred in a wide variety of components for nuclear plants at all stages of construction and operation, that is, shop fabrication, field construction, testing, preoperations, operations, and, on occasion, after shutdown and in storage.

In the late fifties and early sixties, when the reactors being constructed were primarily experimental, incidents of stress-corrosion cracking were generally found to occur in the presence of chlorides or caustic ions. Berry [*1*][2] describes cracking of Types 304 and 347 stainless steels attributed to the presence of chlorides in the Homogeneous Reactor, the Savannah River Reactor, the Nautilus Reactor, the S1W Reactor, the Vallecitos Boiling Water Reactor (BWR), the facility at Capenhurst, England, as well as failures due to caustic attack in the Shippingport Steam Generators. Bush and Dillon [*2*] further describe in a comprehensive report numerous cases of stress-corrosion cracking in reactor components related to contaminants introduced during fabrication or attributed to the environment existing in the reactor. As a consequence of these many failures, considerable effort was made by nuclear steam system suppliers and others through quality control programs to avoid chlorides and other potentially harmful contaminants in subsequent reactors, with reasonable success. Also, the Nuclear Regulatory Commission (NRC) addressed the subject in several regulatory guides [*3,4*] that reference national quality assurance standards on cleaning reactor systems and on packaging, shipping, receiving, storage, and handling nuclear components.

Cracking in Furnace-Sensitized Stainless Steel

In the late sixties, a series of incidents of intergranular stress-corrosion cracking occurred in BWR in severely sensitized austenitic stainless steel components in which the existence of chloride or caustic contaminants was not clearly determined. It was common practice at that time to construct ferritic steel vessels with austenitic stainless steel pipe extensions (safe ends) welded to the nozzles of the vessels that serve as transition pieces to stainless steel piping. These pipe extensions were subjected to the ferritic vessel stress relief treatment, typically as high as 621°C (1150°F) for times up to 10 h. This heat treatment severely sensitized the stainless steel safe ends

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

which, it was later determined, contributed to a rash of cracking incidents due to intergranular stress-corrosion cracking. Two major incidents were the Oyster Creek Nuclear Power Plant [*5*] and the Tarapur Atomic Power Plant [*6*] (India), where extensive cracking was found in sensitized components during the plant installation phase. Cracks were found at locations of high residual stresses in most of the Type 304 stainless steel piping sleeves (stub tubes), through which control rod drives entered the lower head region of the reactor vessels. Extensive cracking was also found in many of the Type 304 stainless steel safe ends attached to the vessel nozzles, as well as several other components. Although the source of corrodent was not established, chlorides from saltwater mists were suspected because of the location of these plants near oceans. Residual fluorides from weld rod coatings were also suspected after it had been shown by Ward et al [*7*] that fluorides would produce intergranular stress corrosion in heavily sensitized Type 304 stainless steel at room temperature. The problem was corrected by either replacing the pipe with Type 304L stainless steel or by grinding out the cracks and cladding the sensitized material with Type 308L stainless steel or Inconel weld material. Cracking of furnace-sensitized stainless steel prior to operation was also reported at the Nuclear Power Reactor (NPR) (Hanford) [*1*], Peach Bottom High-Temperature Gas-Cooled Reactor (HTGR) [*1*], and recently in the Fast Flux Test Facility (FFTF) primary pump [*8*].

Intergranular stress-corrosion cracking in furnace-sensitized piping (safe ends) also occurred after plant operations had started in LaCrosse Boiling Water Reactor (LACBWR) [*9*], Elk River Reactor [*10*], and Nine Mile Point Nuclear Station [*11*], as well as in several European reactors [*2*] (Societa Elettronucleare Nazionale (SENN) in Italy and Dodewaard Reactor in the Netherlands). Such cracking was also found in Dresden 1 [*12*] after seven years of operation in heat-affected zones of welds that were severely sensitized, reportedly by a high-heat-input welding procedure. In these cases, again, no evidence of chloride or caustic contaminant was reported, and the corrodent was probably dissolved oxygen in the high-purity coolant water. These reactors are boiling water reactors, which operate at approximately 288°C (550°F) and 6.9 mPa (1000 psig) and with a reactor coolant of high-purity water, which is maintained through deaerators, filters, and condensate demineralizers. Chloride levels are normally less than 0.02 ppm with higher levels (0.2 to 1 ppm) only permitted for a very limited time. Normal cleanup of the water maintains a neutral pH. Oxygen, formed in these reactors by radiolysis, is stripped during steam generation and removed by means of steam jet air ejectors. Oxygen levels of about 20 ppm occur in the steam and are lowered to approximately 20 ppb in the condensate. During operation, an equilibrium of about 0.2 ppm is maintained in the reactor vessel water phase. This level may rise to approximately 8 ppm if the system is exposed to air at room temperature and pressure during shutdowns.

In most of these incidents, the loadings in the cracked regions of these reactor systems were not high. However, residual stresses which were not well defined probably contributed to these failures since the cracks were all found at locations such as adjacent to welds, in regions of cold-work (grinding) material, or at discontinuities. In LACBWR and Nine Mile Point, severe stressing of the piping was found to have occurred due to mechanical interference to piping expansion, causing circumferential cracks that extended approximately halfway around the pipe on the inside surfaces before propagating to the outer surface and leaking.

In view of the generic nature of this cracking problem and the verification by laboratory tests [*13*] that such intergranular stress-corrosion cracking could occur in pure water with oxygen levels of several parts per million and high stresses (near yield stress levels), additional controls were placed on the design and fabrication of nuclear plants. In plants already constructed, furnace-sensitized Type 304 stainless steel safe ends were with few exceptions removed and replaced with low-carbon stainless steel or by weld material (Type 308L, Inconel weld rod) found not to be susceptible to such cracking. Welding procedures were controlled to minimize heat input, and certain components where cracking had occurred were redesigned to eliminate high stress concentration. Additional controls were added to minimize contamination. NRC issued Regulatory Guides 1.44, "Control of the Use of Sensitized Stainless Steel," and 1.56, "Maintenance of Water Purity in Boiling Water Reactors," to reflect appropriate controls on the condition of the materials and the primary water coolant.

Pipe Cracking Due to Sensitization by Welding

In more recent years, a new series of intergranular stress-corrosion cracks occurred in BWR near welds in nonfurnace-sensitized Type 304 stainless steel pipe containing nonflowing high-purity coolant water. Several small through cracks were first observed in September 1974 in 10.2 cm (4-in.) pipes that bypassed valves in the main recirculating loops at the Dresden Nuclear Power Station Unit No. 2. The cracks were discovered during a search for the cause of an increase in the rate of primary water leakage being measured by a leakage rate surveillance system. Examinations of welds in similar bypass lines at the Quad-Cities Unit Number 2 facility and the Millstone Point Nuclear Plant also revealed a crack in each plant. This situation prompted the Nuclear Regulatory Commission to issue a series of bulletins [*14*] to all 21 BWR facilities that had been licensed at that time, requesting that all welds in such bypass lines be examined for evidence of cracks. As a result of these examinations, which included ultrasonic testing, penetrant testing, and visual examination, additional cracks were found in six different plants at a total of 15 locations. Of the 15 locations, five had through wall cracks, and ten had partial wall cracks initiating on the inner surface. In the subsequent two years, nine more such cracks were discovered.

Coincident with the cracking of the 10.2 cm (4-in.) bypass lines, cracking was observed in two 25.4 (10-in.) core spray injection lines at Dresden Unit No. 2 during a regular inservice inspection of the piping. These core spray lines, also made of Type 304 stainless steel, are used to supply emergency cooling water to the reactor should a loss-of-coolant accident (LOCA) occur. These cracks had all the charcteristics of the cracks in the 10.2 cm (4-in.) bypass lines.

At the onset of this new rash of pipe cracks, investigations were initiated by the NRC (then the Atomic Energy Commission (AEC)), the General Electric Company, The Electric Power Research Institute, and several utility companies. The NRC formed a Pipe Cracking Study Group to investigate the causes, extent, and safety implications of cracking occurrences. General Electric Company conducted extensive laboratory tests and studies on the subject and also established a task group to investigate the broader aspects of the problem and to make assessments and recommendations for ameliorating the problem.

Evaluation of Cracks in Bypass and Core Spray Piping

Both the NRC and the General Electric Company published reports [*15,16*] on their investigations. These studies confirmed that all of the cracks were of the intergranular type, initiating at the inside surface of the pipes and progressing to the outside through regions adjacent to (approximately 0.64 cm (1/4 in.) from) circumferential welds that were slightly sensitized by the weld. The cracks propagated slowly and when leaks developed were still relatively small in size (1.2 to 10.2 cm (1/2 to 4 in.) long on inside diameter (ID)). The leak detection system appears to be a reliable method of detecting the leaking cracks while they are still relatively small. Laboratory work by General Electric indicated that time to initiate and propagate such cracks depended on the level of dissolved oxygen in the water, the degree of sensitization of the steel, and the level of stress (stresses approaching the yield strength of the material were required to cause cracking). The primary and thermal stresses in the piping were analyzed to be well below yield stress. However, the contribution of the residual welding stress was estimated to be high enough to raise the total stress level in localized weld regions to yield levels. Since laboratory tests showed that slightly sensitized stainless steel could be cracked at the 0.2-ppm oxygen level estimated to exist during normal reactor operation, more than enough dissolved oxygen exists in operating BWRs to cause stress-corrosion cracking. Near-stagnant conditions should result in higher levels of oxygen. Conditions conducive to cracking appear to be prevalent in the smaller, thinner pipe. No cracking was found in any of the many thick-walled pipes in the reactor systems, possibly because of lower residual stress levels that reportedly did not coincide with the zone of maximum sensitization, apparently the case in thin pipes. Certain heats of Type 304 stainless steel appear to be more susceptible to stress-corrosion cracking.

It was generally agreed that the cracks found to date did not significantly degrade the structural strength of the pipe enough to compromise the ability of the pipes to perform their function, and, because of the inherent toughness of the material, these cracks would not cause rapid propagating failure resulting in a LOCA. Also, the leakage that occurred was not significant, nor did it release any radiation to the environment. It was also agreed that cracks in these systems can be detected before they grow to sizes that might affect safety and that the probability is extremely low that the presence of cracks or leaks will present a significant safety hazard to the public. However, it was also concluded that the presence of these cracks is undesirable and not consistent with NRC general design criteria and that steps should be taken to avoid or minimize such conditions. It was suggested that this might be accomplished by (*a*) changing to a material more resistant to such stress-corrosion cracking such as clad ferritic steels or the low-carbon grades of austenitic stainless steel, (*b*) wherever possible, improving the control of water chemistry, particularly dissolved oxygen levels, (*c*) reducing residual stresses by controlled welding practice and joint designs, (*d*) reducing cyclic thermal and vibration stresses, and (*e*) tightening leak detection restrictions and in-service inspection requirements for pipe weldment examination.

Present Status of Pipe Crack Problem

Occasional stress-corrosion cracks are still occurring in operating plants in "sensitive" piping such as the bypass lines, core spray lines, and other small, low-flow piping (control rod drive hydraulic return line). These have been located by augmented inspection programs and modified leakage measurement systems. Pipes with cracks and some of those in the more susceptible systems are being replaced, as appropriate, with carbon steel, low-carbon stainless steel, or solution-annealed stainless steel with weld metal "buttered" ends to avoid sensitization during field welding.

The cracking problem has demonstrated a need for additional development work to prevent stress corrosion cracking in nuclear systems. Additional studies are needed to establish alternative materials and conditions that would mitigate this problem. In addition, more quantitative testing techniques that can be applied in the field are needed for locating susceptibility of welded material to such cracking. In this regard, NRC, through the Office of Nuclear Regulatory Research, is supporting the development of an electrochemical technique at the General Electric Company [*17*] for detecting sensitization in austenitic stainless steel that may be applied to welded structures. This technique is presently undergoing shop and field testing. In addition, an ASTM task group under Subcommittee G01.08 on Corrosion of Nuclear Materials is initiating a multilaboratory round-robin testing program to establish the acceptability of this technique for use as an ASTM standard.

Inconel 600 Steam Generator Tubing

Early domestic commercial nuclear power stations were built with austenitic stainless steel steam generators based on its reportedly excellent corrosion resistance, formability, weldability, etc. Three of these early reactors, Shippingport, the Hanford "N" reactor, and Peach Bottom 1, have since been retubed due to cracking and leakage attributed to classical sensitization and chloride and oxygen contamination. Two other plants, Indian Point 1 and Yankee-Rowe, continued to operate with stainless steel tubed steam generators, and presently only Yankee-Rowe is still operative with stainless steel tubes [*18*].

The present vintage of Pressurized Water Reactor (PWR) steam generators, starting approximately in 1967, use Inconel 600 tubing because of its superior resistance to chloride stress-corrosion cracking. However, since its introduction, wastage and intergranular cracking of Inconel 600 has occurred on the secondary side (on the tube outside surface) in plants that have used either sodium phosphate or all volatile water treatment. Secondary side intergranular attack has been attributed to the existence of free caustic; there have also been instances of intergranular stress-corrosion cracking on the tube inside surface (primary side) in relatively pure water. Pure water cracking of highly stressed Inconel is known as the "Coriou effect" [*19*]. In a recent survey [*20*] of 1975 experience in 62 water-cooled nuclear power plants throughout the world, it was found that 22 experienced steam generator tube failures, most of which were due to corrosion.

Steam Generator Designs

In PWR steam generators, the heat from the primary coolant is used to produce steam, which passes through the turbine generators to the condenser where the waste heat is removed. There are two typical current designs, the vertical U-tube natural circulation boiler and the so-called once-through design which is a straight-tube, straight-shell, counterflow heat exchanger that provides superheated steam to the turbine.

The steam generator tubing is Inconel 600, and the tube shells are carbon steel with, on the primary side, an Inconel 600 cladding to which the tubes are welded. To restrain the tubes from vibration, a series of carbon steel supports are used for the straight portions of the tubes, and for the U-tube design, a series of restraints in the form of antivibration bars are used for the curved portion of the tubes.

The steam generator tubing diameter and wall thickness vary according to the particular design and range from 0.625 to 0.875 in. diameter with 0.034 to 0.050-in. wall.

Both design features and environmental factors have had a pronounced influence on the integrity of steam generator tubing. Impurities in the secondary water, which are allowed to concentrate because of thermal/hydraulic factors that result in regions of low flow, have caused steam generator tube degradation. The main sources of these impurities are corrosion of materials in the turbine, condenser, and feedwater piping and inleakage of the tertiary coolant into the condenser.

Secondary Water Chemistry

The underlying philosophy in secondary water chemistry is to minimize corrosion and prevent scale formation on the high-heat-flux surface of the tubing by the impurities. There are three types of water chemistries presently in use in PWR secondary water systems (*a*) an all volatile treatment (AVT), in which the pH of the deionized water in the steam generator is raised and the oxygen scavenged by volatile additives such as hydrazine or morpholine, (*b*) a coordinated phosphate treatment, in which sodium phosphates are added to the coolant to raise the pH and react with scale-forming impurities to produce relatively harmless soft phosphate precipitates, coupled with additions of hydrazine, morpholine, or sodium sulfite to scavenge the oxygen, and (*c*) a zero-solids treatment (ZST), which utilizes full-flow condensate demineralization with AVT to remove caustic-forming impurities and scale-forming solids from the steam generator.

Phosphate Chemistry and Wastage and Cracking

For many years, the sodium phosphate treatment was widely used for U-tube steam generators that remove precipitated or suspended solids by blowdown. It was successful as a scale inhibitor; however, in the early use, many PWR steam generators with Inconel 600 tubing experienced stress-corrosion cracking [*21*]. The cracking was attributed to free caustic which can be formed when the sodium (Na/PO_4) ratio exceeds the recommended limit of 2.6. In addition, some of the insoluble metallic phosphates formed by the reaction of sodium phosphates with the solids in the feedwater are not adequately removed by blowdown. They tend to accumulate as sludge on the tube sheet and tube supports at the central portion of the tube bundle where restricted water flow and high heat flux occurs. Phosphate concentration (hideout) at crevices in areas of the steam generator noted previously caused localized wastage resulting in thinning of the tube wall.

The problem of stress-corrosion cracking was corrected by maintaining the Na/PO_4 ratio between 2.6 and 2.3. Although the recommended Na/PO_4 ratio was maintained, it did not correct the phosphate hideout problem that caused wastage of the Inconel 600 due to local concentration of residual acidic phosphates that are not removed by blowdown.

Because of problems encountered with the phosphate treatment, most PWRs using phosphate treatment for their secondary coolant shifted to AVT chemistry. It was found that wastage sometimes continues after termination of the phosphate feed to the secondary coolant and is attributed to the residual phosphates and sludge not removed by blowdown. Stress-corrosion cracking also occurs (after termination of the phosphate feed) when the Na/PO_4 ratio rises above 2.6 due to "inverse hideout" of the residual phosphates. Resolution of these phosphates produced free caustic conditions in the secondary coolant. Condenser inleakage will also contribute to the caustic buildup.

All Volatile Treatment and "Denting"

A new form of tube degradation called "denting" started to manifest itself at plants that switched from phosphate treatment to AVT for their secondary water [22]. Denting is a reduction of the outside diameter (OD) of the tubing which occurred at the tube locations where the tube passes through the support plates. It is generally agreed that denting is associated with expansion of the carbon steel support plate corrosion products and the resulting forces on the steam generator tubing.

It is presumed that the annulus between the tube and tube support plate is filled initially with a phosphate deposit during the period of phosphate water treatment. After the change to AVT, an ingress of Cl^- from leaking condenser tubes at brackish or seawater locations results in acid conditions in the crevice causing runaway formation of magnetite on the carbon steel support plates in the annuli. This is followed by denting.

In certain locations of the support plate, continued denting leads to tube deformation and initiation of intergranular penetration from the tube inside surface. These intergranular cracks have resulted in the development of leaks.

Denting has also resulted in deformation of all the support plates, with deformation of the topmost support plates resulting in dynamic straining of those tubes with the tightest U-bends. This dynamic straining plus the residual stress from the tube bending and the normal operational thermal and pressure stress have resulted in intergranular attack and cracking from the inside surface of the tight-bend U-tubes at the apex of the bend. In both of these cases, no corrodent has been identified, although there have been previous reports of cracking of highly stressed Inconel in primary water.

Zero Solids Treatment and Fatigue Cracks

No stress-corrosion cracking or wastage of steam generator tubes has occurred with the use of ZST for the secondary coolant. Although the once-through generators, which primarily use ZST, have recently experienced limited steam generator tube cracking of a localized nature attributed to high-cycle fatigue, no corrosion mechanism has been reported operative [*23*].

Role of the U.S. Nuclear Regulatory Commission

The NRC is concerned about steam generator tube integrity from a safety viewpoint. Stress-corrosion cracking or wastage that has penetrated a significant portion of the tube wall thickness could impair tube structural integrity. Stress-corrosion cracks propagating through the tube wall cause leakage of the primary coolant, releasing radioactivity products into the PWR secondary system. In the event of a steam line break, partial through-wall cracks could cause tube rupture, resulting in unimpeded flow of the primary coolant. Localized wastage-type corrosion leads to thinning of the tube wall, which could lower tube strength and cause tube collapse during a LOCA, resulting in contamination of the primary coolant.

Analyses and laboratory tests have shown that steam generator tubes with defect penetrations ≤ 50 percent of the tube wall thickness will maintain tube integrity, under all the mechanical and thermal forces associated with a postulated LOCA plus safe shutdown earthquake, steam line, or feedwater line rupture. The setting of a 50 percent limit on minimal acceptable tube wall thickness ensures that tubing will withstand with adequate margin the maximum imposed stress during normal operation without exceeding the yield strength of Inconel 600 and have a margin of at least 3 between the maximum internal pressure imposed during normal operation and tube burst pressure.

The NRC has issued two regulatory guides addressing steam generator tube integrity. Regulatory Guide 1.83, "Inservice Inspection of PWR Steam Generator Tubes" [*24*], includes recommendations for an eddy-current inspection program intended to monitor the condition of steam generator tubes. Involved are an extent and frequency of examination considered essential to detect degradation on a scheduled basis with more frequent inspections of those plants where problems have been experienced. An eddy-current examination method to be used for these inspections is included in Section XI of the American Society of Mechanical Engineers (ASME) code and is mandatory for all inservice inspections [*25*].

In Regulatory Guide 1.121, "Bases For Plugging Degraded Steam Generator Tubes" [*26*], criteria for plugging degraded tubes are established, based on the calculation of the minimum tube wall thickness required for continued service. Degraded tubes found by eddy-current inspection to exceed this level will require plugging by a manual welding or explosive plugging technique.

Inconel tube manufactured to ASTM Specification for Nickel-Chromium-Iron Alloy (UNS N06600) Seamless Pipe and Tube B-167 is ultrasonically examined in accordance with ASTM Method for Ultrasonic Inspection of Metal Pipe and Tubing (E 213-77) for flaws and in addition is also inspected by eddy-current techniques.

Steam generators that are eddy-current inspected shortly before initial plant startup (baseline inspection) have demonstrated that no indications had escaped the tube manufacturer's inspection. Eddy-current signals from tubes that were abused in tubing and fabricating the steam generator were noted in a few instances, but, because of design conservatism, this type of defect has not been shown to cause failure during operation.

According to Regulatory Guide 1.83, the first inservice examination is performed during the first refueling outage, which, for the PWR plant presently on line or being constructed, occurs in the one-to-two-year interval following placement into commercial service. The second examination is performed within an additional period of from one to two years. Further along in the service life of the plant, if degradation has not exceeded the degree shown in the next paragraph, the third and subsequent examinations can be extended to periods of three and one-third years.

If the steam generator tubes examined in an inspection exhibit indications in excess of 20 percent of the wall thickness in more than 10 percent of the tubes examined, the subsequent two inspections revert to the one-to-two-year inspection interval. The three and one-third year inspection interval can be resumed only after no more than 10 percent of the tubes examined exhibit either new or additional degradation.

The regulatory guides addressing both inspection and plugging are being revised to reflect the most recent operating experience and address some of the newer problems of denting and intergranular attack on the tube inside surface (primary water) plus the use of advanced eddy-current methods, including multifrequency systems, for determining type and extent of defects.

Role of ASTM

NRC has requested the American Society For Testing and Materials to establish a test procedure for determining the susceptibility of Inconel 600 to stress-corrosion cracking in water environments.

An ASTM task group under G01.08 Corrosion of Nuclear Materials has been convened and is addressing the problem.

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Comparative Methods for Measuring Degree of Sensitization in Stainless Steel

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REFERENCE: Clarke, W. L., Cowan, R. L., and Walker, W. L., "**Comparative Methods for Measuring Degree of Sensitization in Stainless Steel,**" *Intergranular Corrosion of Stainless Alloys, ASTM STP 656*, R. F. Steigerwald, Ed., American Society for Testing and Materials, 1978, pp. 99-132.

ABSTRACT: Three test methods for determining degree of sensitization in austenitic stainless steels have been investigated. The results clearly show that all three test methods are capable of detecting moderate-to-severe degrees of sensitization, but the electrochemical potentiokinetic reactivation technique is the most sensitive for quantitatively determining the levels of sensitization which are of primary concern for industrial use. Both the ASTM Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels (A 262-75, Practice A) and the electrochemical potentiokinetic reactivation methods appear to saturate at high degrees of sensitization, which results in a loss of discriminating power between different heats of material. While the A 262, Practice E, method does not appear to saturate and retains its discriminating power at high degrees of sensitization, it is not a suitable method for detection at the lower degrees. Of the three test methods, it appears that the electrochemical potentiokinetic reactivation test is the most suitable for determining the quantitative degree of sensitization over the levels of industrial concern.

KEY WORDS: stainless steels, intergranular corrosion, sensitizing, electrochemistry, strains, loads, stress corrosion cracking

The accepted ASTM Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels (A 262-75, Practices A,E) used to detect sensitization have three major deficiencies: (*a*) they do not readily quantify the degree of sensitization, (*b*) they are not rapid (with the exception of ASTM A 262, Practice A), and (*c*) they are destructive (with the exception of A 262, Practice A). The accepted practices were developed to screen materials that would be subjected to highly corrosive environ-

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ments which could cause severe general intergranular attack in heavily sensitized austenitic stainless steels. In recent years, experience has shown that "moderately" sensitized materials can undergo intergranular stress-corrosion cracking (IGSCC) in environments that do not cause appreciable intergranular attack in the absence of stress [*1*].[3] Thus, a more discerning test is required for these applications. Conversely, there are applications where the use of moderately sensitized material, which could not pass the current practices for determining the presence of sensitization, would perform satisfactorily in the service environment [*2*]. In these cases, a manufacturer would be forced to use an extra-low-carbon or stabilized grade of material, with the associated cost or strength penalties. A test that measured the degree of sensitization, in conjunction with calibration tests in the service environment, could provide a "go/no go" materials acceptance criteria for both cases. A rapid nondestructive test would also to helpful for quality control on shop- or field-constructed components which receive thermal treatments during fabrication.

In this paper, progress in establishing a quantitative test method for measuring degree of sensitization is described. Three techniques were investigated: (*a*) modified A 262, Practice A, (*b*) modified A 262, Practice E, and (*c*) an electrochemical reactivation method. A fourth technique, a dynamic straining stress corrosion test [*3*] was used as a reference method to determine the effect of moderate amounts of sensitization on IGSCC. In this referee test, dynamic straining coupled with a very severe environment (550°F high-purity water containing 8-ppm O_2) can cause intergranular fracture of mildly sensitized stainless steel.

Experimental Procedures

Materials

There were thirteen heats of AISI Type 304 stainless steel used in the sensitization measurements program. These heats included five heats of 10.2 cm (4 in.), Schedule 80 seamless piping; one heat of 25.4 cm (10 in.), Schedule 80 and two heats of 15.2 cm (6 in.), Schedule 80 seamless pipe; one heat of 66 cm (26 in.), Schedule 80 rolled and welded pipe; one heat each of 2.5 cm (1 in.) thick forged bar, forged plate, and hot-rolled plate; and one heat of 3.1-cm (1¼-in.) bar. The chemical composition and mechanical properties for these materials are given in Tables 1 and 2, respectively.

For the bulk of the study, specimens from twelve heats were tested in the as-received (mill-annealed (MA)) condition and, after a low-temperature sensitization (LTS) treatment at 500°C (932°F) for 24 h in air, followed

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[3] The italic numbers in brackets refer to the list of references appended to this paper.

TABLE 1—*Composition of steels used in sensitization program (element, percent, nd = not determined).*

Heat	C	Cr	Ni	Mn	Si	Mo	Cu	S	P	N
M7616[a]	0.060	18.68	10.16	1.69	0.50	0.08	0.08	0.012	0.022	0.038
812292[b]	0.069	18.18	9.14	0.74	0.58	0.19	0.17	0.014	0.019	0.034
78500[c]	0.043	19.06	8.88	1.64	0.55	0.04	0.42	0.012	0.016	0.073
8082228[d]	0.055	18.22	8.65	1.74	0.57	0.38	0.30	0.013	0.030	nd
M7772[a]	0.050	18.81	10.15	1.80	0.38	0.11	0.15	0.015	0.026	0.034
TH6656[e]	0.060	18.31	9.30	1.72	0.47	0.24	0.25	0.006	0.024	0.030
454659[a]	0.045	18.40	9.76	1.25	0.57	0.23	0.07	0.015	0.018	0.029
834264[f]	0.060	18.30	9.12	1.58	0.62	0.30	0.09	0.028	0.030	nd
27388[c]	0.044	18.86	8.76	1.77	0.60	0.11	0.49	0.010	0.019	0.072
2P6396[a]	0.040	18.66	10.30	1.65	0.53	0.20	0.12	0.016	0.022	0.033
2P6424[a]	0.040	18.37	9.61	1.65	0.46	0.25	0.08	0.013	0.021	0.038
159340[g]	0.070	18.32	9.35	1.75	0.40	0.41	0.10	0.017	0.035	nd
X14902[h]	0.065	18.68	9.20	1.75	0.48	nd	nd	0.028	0.029	nd

[a] 4-in., Schedule 80 seamless pipe.
[b] 1 by 4-in. forged bar.
[c] 6-in., Schedule 80 seamless pipe.
[d] 1-in., hot-rolled plate.
[e] 10-in., Schedule 80 seamless pipe.
[f] 26-in., rolled and welded pipe.
[g] 1 by 12-in. forged plate.
[h] 1¼ by 1-in. bar.

Metric conversion: 1 in. = 2.5 cm.

TABLE 2—*Mechanical properties of steels used in sensitization studies* (*nd* = *not determined*).

Heat	Room Temperature		289 °C (550 °F)					
	YS (ksi)	UTS (ksi)	*E* (%)	RA (%)	YS (ksi)	UTS (ksi)	*E* (%)	RA (%)
M7616	41.6	91.9	73.5	74.9	28.8	69.4	40.3	71.7
812292	36.4	91.4	82.9	81.7	30.0	66.8	44.3	73.8
78500	35.2	86.0	83.3	81.7	17.8	61.5	51.4	72.5
8082228	41.9	92.9	75.5	75.0	26.3	69.6	46.9	64.4
M7772	41.1	92.4	68.3	78.1	28.5	69.7	40.2	72.1
TH6656	37.0	90.1	66.8	83.4	24.1	66.1	39.1	75.6
454659	35.4	90.4	60.6	79.3	25.9	66.7	34.2	70.7
834264	38.5	89.5	66.0	70.0	nd	nd	nd	nd
27388	39.3	90.7	77.1	77.3	22.7	64.3	49.0	75.2
2P6396	38.4	87.7	75.8	78.5	24.2	65.3	42.3	72.7
2P6424	39.0	89.6	74.3	81.6	26.1	66.0	42.5	75.5
159340	35.1	90.4	77.6	75.8	24.0	68.3	48.1	70.6
X14902	38.2	92.5	76.3	81.5	26.2	67.8	41.6	75.6

by furnace cooling. This treatment was used to produce light degrees of sensitization to test the sensitivity of the various methods. Specimens from two heats (M7616 and 27388) were also tested after solution annealing at 1038°C (1900°F) for 1 h and water quenching, followed by the LTS treatment. Additionally, one specimen from heat M7616 was tested in the solution-annealed condition (solution-annealed treatment just described), without a sensitization heat treatment.

In addition, two smaller studies were performed to investigate the effects of more severe sensitization treatments. In one series of tests, specimens from six piping heats were evaluated after sensitizing 40 h at 620°C (1150 °F); the other study was conducted on specimens from a single heat of bar stock (Heat X14902). These specimens were sensitized 1, 4, 20, and 40 h at 620°C (1150°F).

Measurement of Sensitization

ASTM A 262, Practice A—All test specimens were evaluated for percent ditching after oxalic acid etching according to ASTM A 262, Practice A, modified according to the procedure given in Appendix I. The modification of the ASTM practice consisted of measuring and reporting the amount of grain boundary length that showed a ditched structure. The specimens examined were those already mounted which were repolished after electrochemical potentiokinetic reactivation (EPR) testing (discussed later).

ASTM A 262, Practice E—Companion specimens to those used for the A 262, Practice A, and electrochemical tests were also evaluated for sensitization using two modifications of A 262, Practice E, the acidified copper-copper sulfate test. The conventional A 262, Practice E, test gives "go/no go" results, that is, either the specimen exhibits fissuring when bent, or it does not. The first modification used was to obtain semiquantitative data by accurately measuring maximum penetration depths on tension specimens which were strained 3 to 5 percent after exposure to the test solution, and then examining metallographically prepared specimens (Appendix II).

The second method consists of measuring the penetration which occurs during the test period by means of the change in effective cross-sectional area of the specimen, by comparison of the ultimate tensile strength of the tested specimen to a specimen of the same material which has not been exposed to the test solution [*4*]. This treatment of the data results in a true measure of penetration during the test, regardless of grain fallout (Appendix II).

EPR Measurements—The degree of sensitization was quantified using the recently developed EPR method. This methed consists of developing potentiokinetic curves of a polarized specimen obtained by controlled potential sweep from the passive to the active region (reactivation) in a specific electrolyte; details of the test technique have been reported [*5,6*], and are presented in specification form in Appendix III. The test conditions used for the EPR measurements are given in Table 3. The criteria used to distinguish between annealed and sensitized specimens include the activation charge, Q, given by the integrated area below the reactivation peak of the curve (Fig. 1). Sensitized steels are easily activated and show high Q values, compared to annealed steels which are not susceptible to intergranular corrosion. The value Q is normalized by both specimen size and grain size as described in Appendix III. The data normalized in this fashion are called P_a and represent the charge per square centimetre of grain boundary area. This treatment of the data permits normalized direct comparisons of different heats of material which exhibit different Q values solely as a result of differences in grain size. This topic has been described in detail [5].

The EPR specimens were 0.3 by 0.3-cm sections cut from the tab ends of the uniaxial tension specimens tested for IGSCC resistance. The specimens were mounted in a Maraglas compound, so that only one face of the specimen was exposed. Electrical contact was made by spot-welding a stainless steel screw to each specimen before mounting. Finally, the mounted specimens were polished before testing so that the effect of the test (grain boundary attack) could be viewed and documented metallographically.

IGSCC Tests—The susceptibility to IGSCC was determined by conducting dynamic strain tests [*1,3*] in 289°C (550°F) high-purity (approximately 1 μS) water containing 8-ppm dissolved oxygen. This is a very severe test and does not usually represent an environment of industrial interest. However, this extreme case was used in this investigation to maximize the potential for correlation between sensitization and IGSCC testing. In the application of these tests in industrial practice, the type correlation performed in this study would have to be undertaken in test environments of industrial interest. In this test, uniaxial tension test specimens are slowly strained to failure at 0.0008 mm/min (0.032 mil/min) in the environment. Susceptible materials generally reveal shorter failure times, lower breaking stresses, and lower reduction-in-area (RA) values compared to similar tests performed in air or inert gas. In addition, the data generated can be treated to obtain a susceptibility index, I_{DS}, with the expression

$$I_{DS} = 1 - \frac{\sigma_W(1 + E_W)}{\sigma_A(1 + E_A)}$$

where

σ_W = maximum breaking stress in water with O_2,
σ_A = maximum breaking stress in air,
E_W = elongation in water, and
E_A = elongation in air.

TABLE 3—*EPR test conditions.*

Electrolyte	0.5 M H_2SO_4 + 0.01 M KCNS
Temperature	30°C
Specimen surface finish	1 μm (diamond paste)
Reactivation sweep rate	6 V/h (cathodic)
Passivation potential time	+ 200 mV/2 min
Deaeration	N_2
Polarization system	Hokuto-Denko with Princeton Applied Research Coulometer
Data normalization	P_a (C/cm^2) = Q (C)/GBA (cm^2)[a]

[a] GBA = calculated grain boundary area in sample (see Appendix III).

Greater susceptibility to IGSCC is indicated as I_{DS} approaches a value of 1. Finally, the failure mode is documented by scanning electron microscopic and metallographic examination of the fractured specimens. Test specimen gage length is typically 1.9 cm (0.75 in.).

Results

The results of the study to evaluate degree of sensitization in twelve heats of Type 304 stainless steel in the mill-annealed condition, and after sensitizing 24 h at 500°C, are given in Table 4. Specimens from seven of the

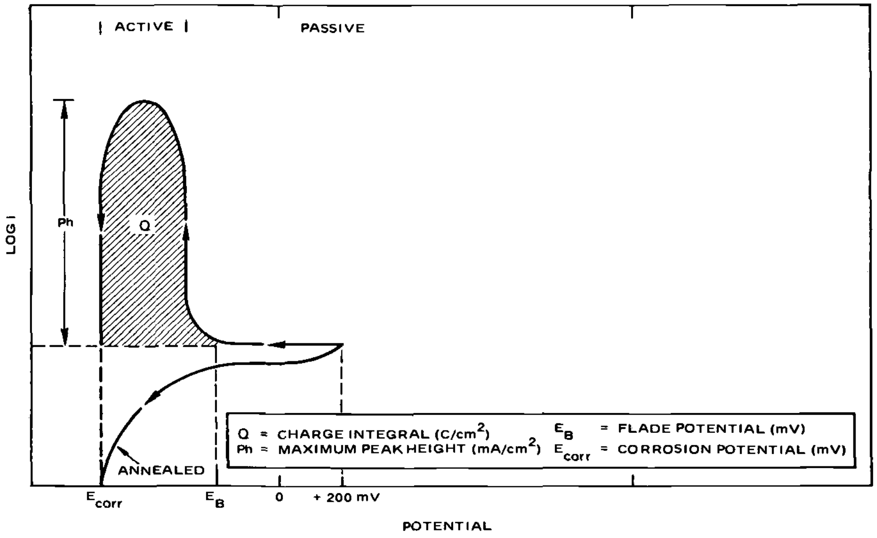

FIG. 1—*Schematic of reactivation polarization curve showing parameters of interest for EPR testing.*

TABLE 4—*Summary of data developed to compare three methods for measuring degree of sensitization in Type 304 stainless steel with IGSCC susceptibility.*

Material Identification			Degree of Sensitization[a]			IGSCC Susceptibility after Dynamic Strain	
Heat	Product	Condition[b]	A 262-A (% Ditch)	A 262-E (mils)	EPR (C/cm^2)	I_{DS}	IGSCC[c]
M7616	Seamless pipe, 4-in., Schedule 80	SA	. . .	<0.1	0.0	0.20	no
		SA + LTS				0.37	no
		MA	40	0.2	7.3	0.69	yes
		MA + LTS	50	0.4 to 0.8	40.0	0.92	yes
812292	Forged bar, 1-in.	MA	≤1	<0.1	2.0	0.51	no
		MA + LTS	≤1	0.1 to 0.4	16.8	0.75	yes
78500	Seamless pipe, 6-in., Schedule 80	MA	≤1	<0.1	1.8	0.38	no
		MA + LTS	≤1	0.4 to 0.8	12.0	0.65	yes
8082228	Hot rolled plate, 1-in.	MA	≤1	<0.1	0.4	. . .	. . .
		MA + LTS	≤1	0.4 to 0.8	7.4	0.82	yes
M7772	Seamless pipe, 4-in., Schedule 80	MA	≤1	<0.1	0.0	. . .	. . .
		MA + LTS	≤1	0.2 to 0.4	6.7	0.52	no
TH6656	Seamless pipe, 10-in, Schedule 80	MA	2	<0.1	0.0	. . .	. . .
		MA + LTS	14	0.2 to 0.8	6.5	0.65	yes
454659	Seamless pipe, 4-in., Schedule 80	MA	≤1	<0.1	0.0	. . .	. . .
		MA + LTS	≤1	0.8 to 1.6	7.3	0.77	yes
834264	Rolled and welded pipe, 26-in., Schedule 80	MA	5	0.1	0.7	0.53	no
		MA + LTS	25	0.1 to 0.2	4.6	0.71	yes
27388	Seamless pipe, 6-in., Schedule 80	SA	≤1	<0.1	0.0	0.36	no
		MA	≤1	<0.1	0.4	0.59	no
		MA + LTS	≤1	0.8 to 1.6	4.2	0.42	no
2P6396	Seamless pipe, 4-in., Schedule 80	MA	≤1	<0.1	0.0	. . .	. . .
		MA + LTS	≤1	0.4 to 0.8	4.0	0.44	no
2P6424	Seamless pipe, 4-in., Schedule 80	MA	≤1	<0.1	0.2	. . .	. . .
		MA + LTS	≤1	0.1 to 0.2	2.6	0.53	no
159340	Forged plate, 1-in.	MA	≤1	0.1	0.0	. . .	. . .
		MA + LTS	≤1	0.1 to 0.2	2.7	0.55	no

[a] ASTM A 262, Practice E pulled 3 to 5 percent in tension after three 72-h exposures. EPR at 6 V/h and 30°C in 0.5 *M* H_2SO_4 + 0.01 *M* KCNS (GBA adjusted).

[b] Solution annealed (SA) = 1038°C (1900°F) / 1 h/water quenched, MA = mill annealed, LTS = 500°C (932°F) / 24 h/furnace cooled.

[c] SEM examination of fracture surfaces.

Metric conversion: 1 in. = 2.5 cm.

twelve heats indicated IGSCC susceptibility after dynamic strain testing, with an I_{DS} value of 0.65 established for this heat treatment in this environment as the lower limit for susceptibility. The most extensive IGSCC noted occurred in one of the 10.2-cm (4-in.) seamless pipe heats (M7616), where IGSCC occurred even in the mill-annealed condition (Fig. 2) in this severe environment. The mill-annealed specimen did reveal some mixed mode cracking (intergranular plus transgranular), but crack initiation was always intergranular. This particular heat of material was also extremely susceptible to IGSCC in other studies [*3,5*] using more severe sensitization treatments. This level of susceptibility would have been predicted by degree of sensitization measurements using both A 262, Practice A, and the EPR technique. But, the EPR method provides quantitative data relative to the level of susceptibility between mill-annealed and sensitized conditions (P_a = 7.3 and 40.0 C/cm^2 compares to I_{DS} = 0.69 and 0.92, respectively), while the A 262, Practice A method shows little differentiation (40 and 50 percent ditching). The etch structures developed after the A 262, Practice A, and EPR exposures are shown in Figs. 3 and 4, respectively. As shown in Fig. 3, the extent of grain boundary ditching appears comparable for both conditions; however, the EPR-produced structures (Fig. 4) clearly delineate the difference in grain boundary attack (chromium depletion around carbide particles) [*5*] between the mill-annealed and lightly sensitized condtion.

In contrast, the A 262, Practice E, test does not appear very sensitive at these lower degrees of sensitization. The structures developed in the mill-annealed and sensitized specimens after three 72-h exposures are shown in Fig. 5, where penetration depths after straining 3 to 5 percent can only be measured with great difficulty. Based on the data developed by A 262, Practice E, for the other eleven heats, the difference between penetration depths of 0.2 mil for the mill-annealed condition and 0.4 to 0.8 mil after sensitizing do not appear significant.

The 25.4-cm (10-in.) seamless pipe heat (TH6656) revealed the lowest level (I_{DS} = 0.65) of IGSCC after sensitizing of the seven susceptible materials; this material was not susceptible in the mill-annealed condtion. The fracture surface for this specimen after dynamic strain testing is shown in Fig. 6. Only one corner of the specimen revealed IGSCC; the remainder of the specimens failed ductilely (approximately 90 percent of the fracture surface reveals IGSCC in highly susceptible materials after severe sensitization treatments) [*3*]. This specimen also contained only a few secondary cracks, while highly susceptible materials, such as Heat M7616, usually develop secondary cracking too numerous for counting.

The etch structures produced in the sensitized Heat TH6656 specimen during degree of sensitization measurements using the three methods are shown in Fig. 7. Again, the A 262, Practice E, results are not sufficiently discerning to predict the IGSCC behavior. Both the A 262, Practice A, and EPR method reveal a sensitized microstructure, but only the EPR measure-

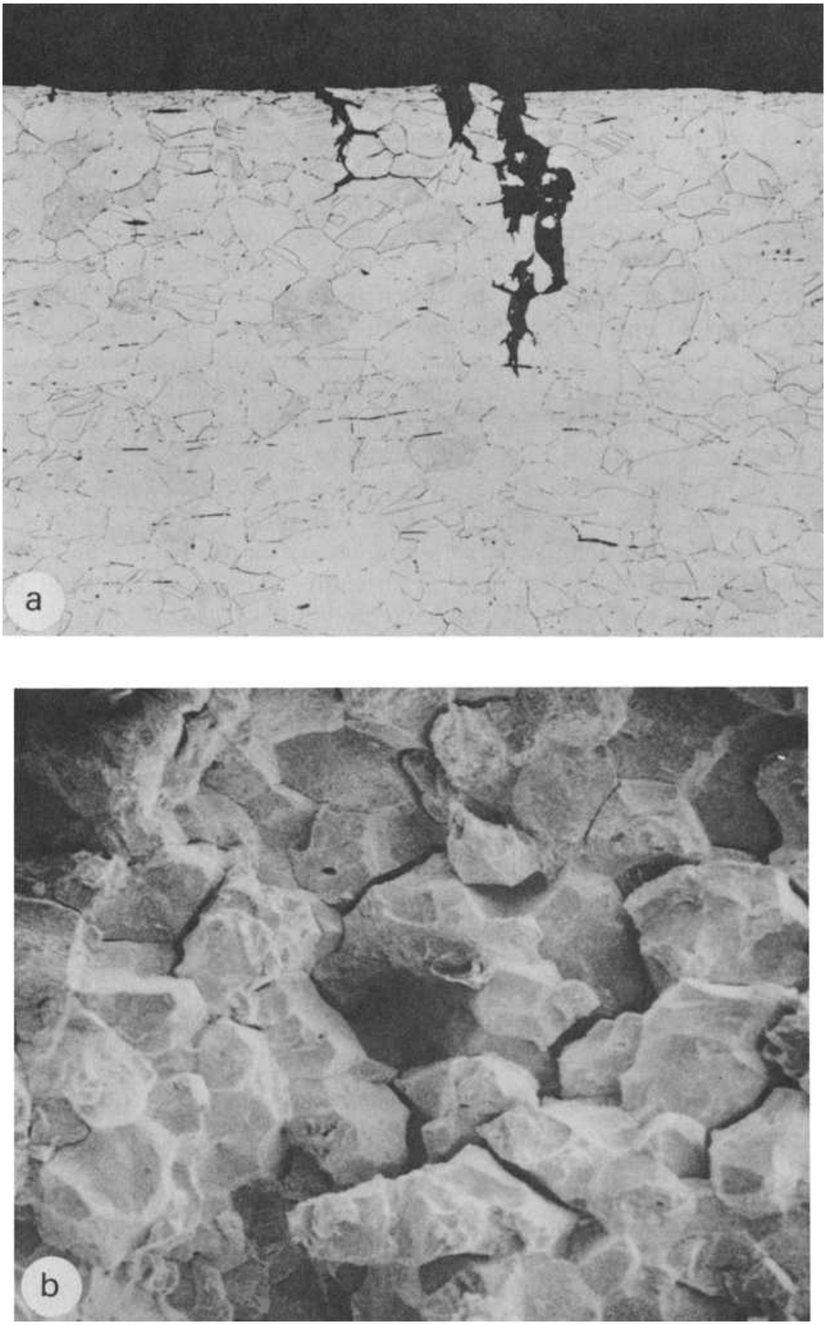

FIG. 2—*Stress-corrosion cracking in Type 304 stainless steel (Heat M7616) tested by dynamic strain in 289°C water with 8-ppm* O_2 *at extension rate of 0.0008 mm/min:* (a) *mill annealed,* ×*100,* (b) *sensitized 24 h at 500°C, SEM,* ×*200.*

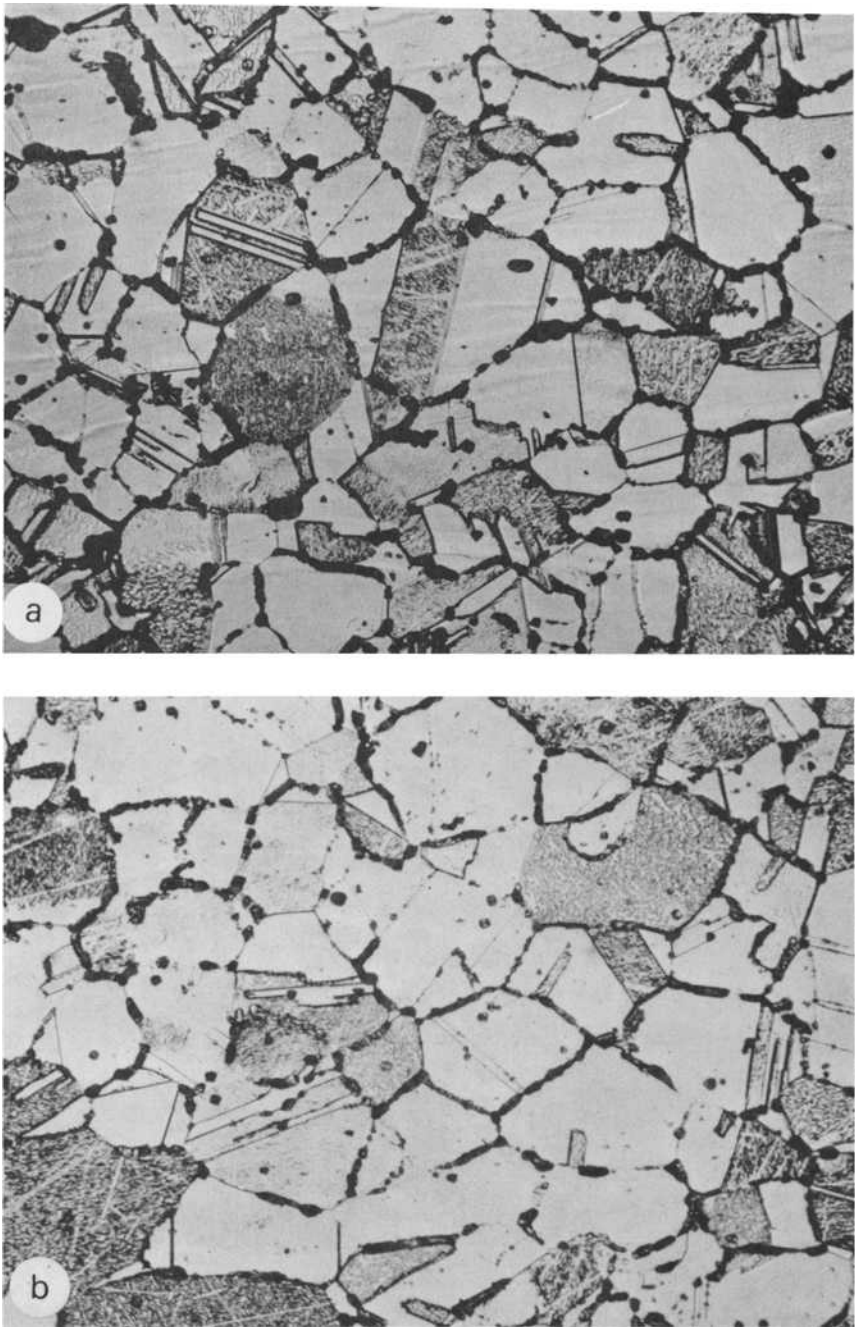

FIG. 3—*ASTM A 262, Practice A etch in Type 304 stainless steel (Heat M7616):* (a) *mill annealed (40 percent ditching), ×250,* (b) *sensitized 24 h at 500°C (50 percent ditching), ×250.*

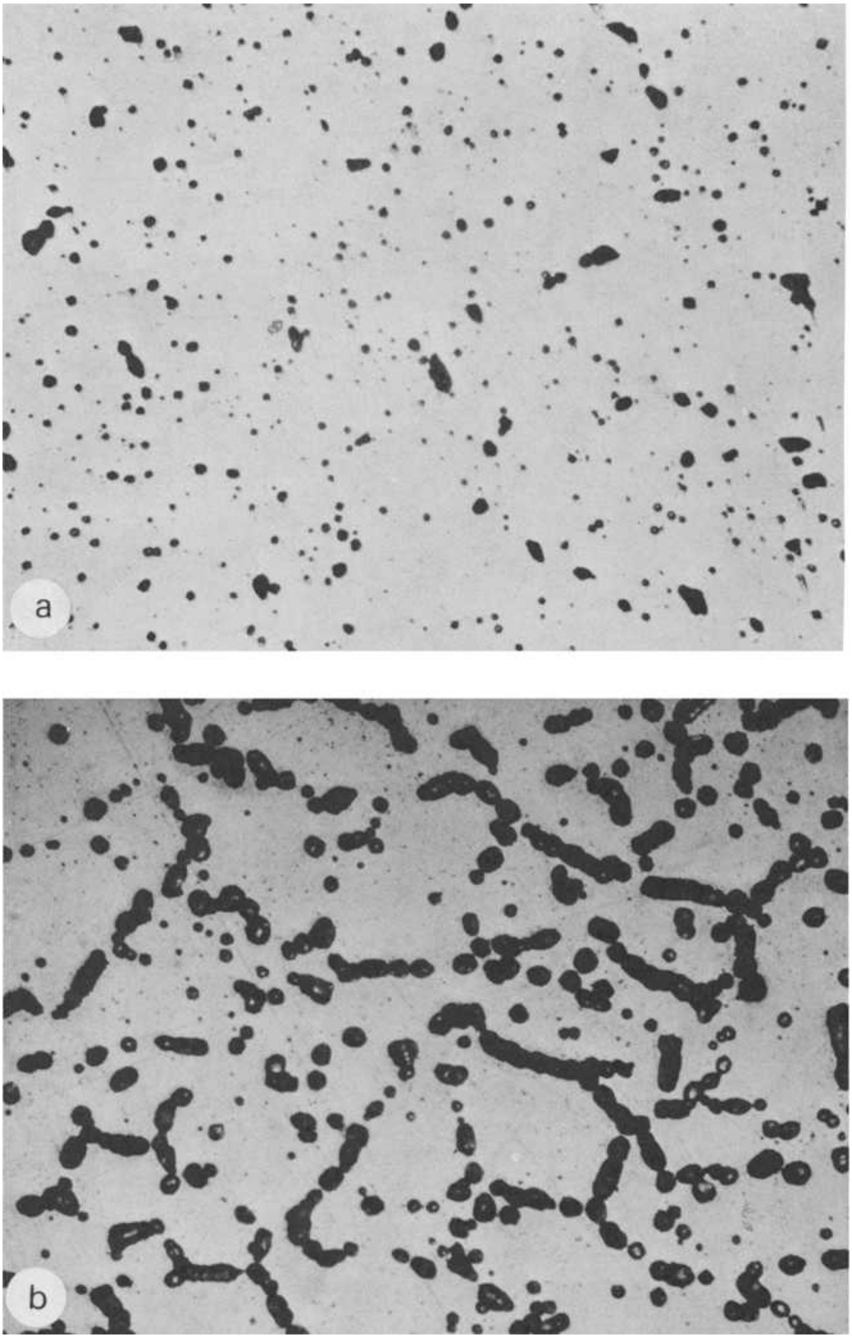

FIG. 4—*Etch structure in Type 304 stainless steel (Heat M7616) after EPR testing in 0.5* M H_2SO_4 + *0.01* M *KCNS at 30°C*: (a) *mill annealed* ($P_a = 7.3\ C/cm^2$), ×*250,* (b) *sensitized 24 h at 500°C* ($P_a = 40\ C/cm^2$), ×*200.*

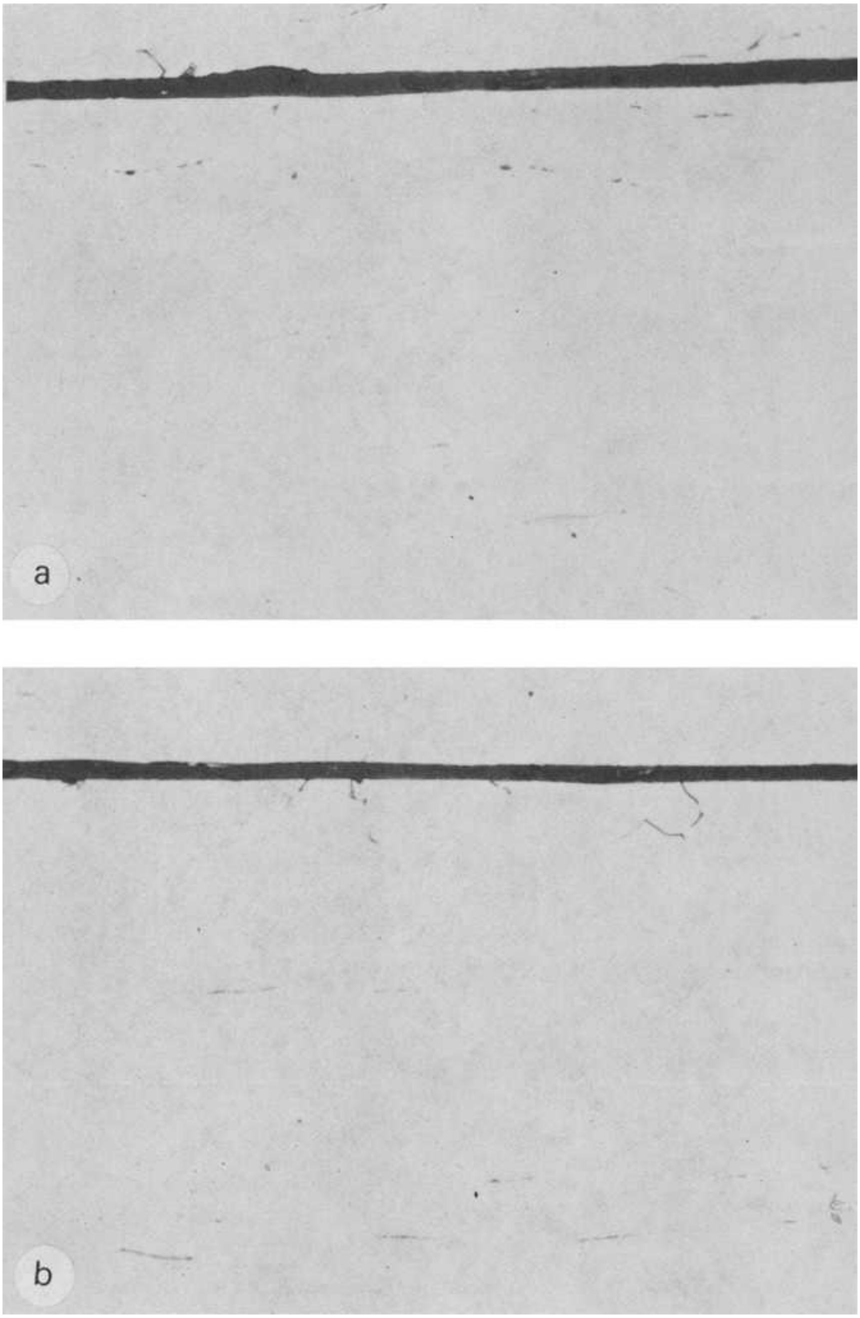

FIG. 5—*ASTM A 262, Practice E attack in Type 304 stainless steel (Heat M7616) after three 72-h exposures (pulled 3 to 5 percent in tension):* (a) *mill annealed (0.2 mil penetration),* ×*250,* (b) *sensitized 24 h at 500°C (0.4 to 0.8 mil penetration),* ×*250.*

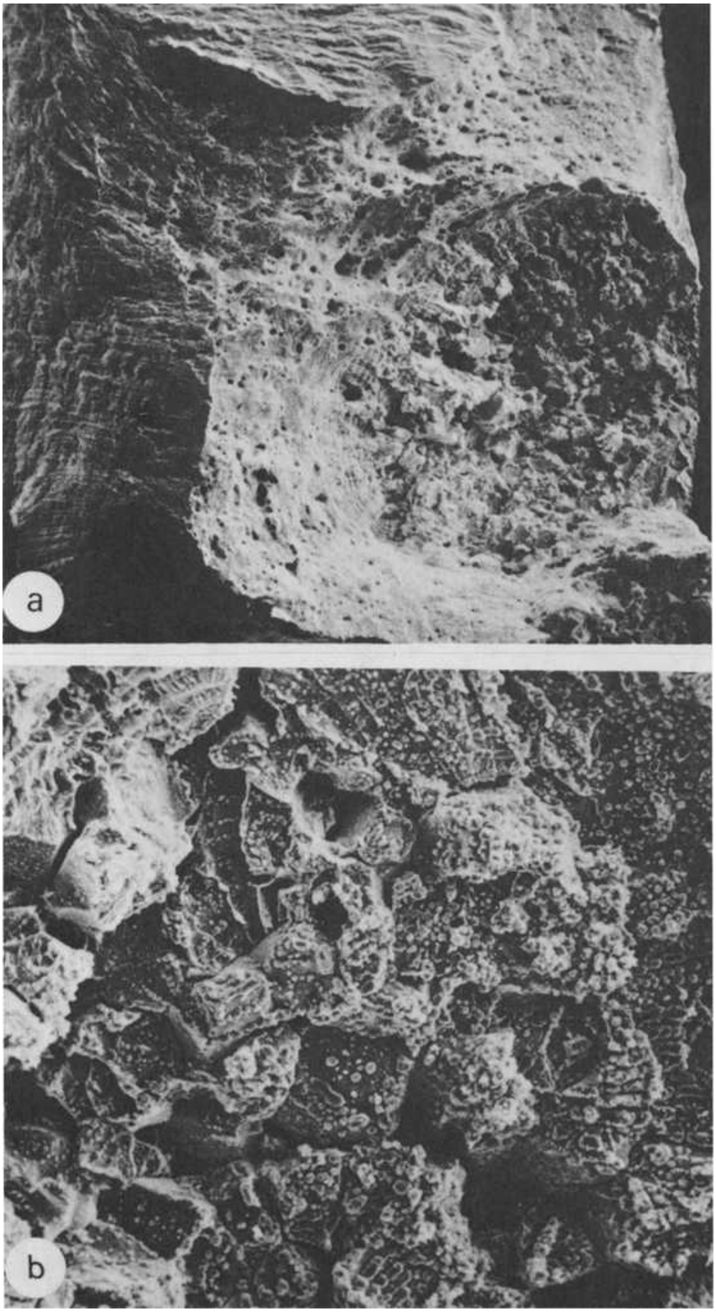

FIG. 6—*Fracture surface of sensitized (500°C/24 h) Type 304 stainless steel seamless pipe (Heat TH6656) tested by dynamic strain in 289°C water with 8-ppm* O_2 *at an extension rate of 0.0008 mm/min:* (a) ×*40,* (b) ×*300.*

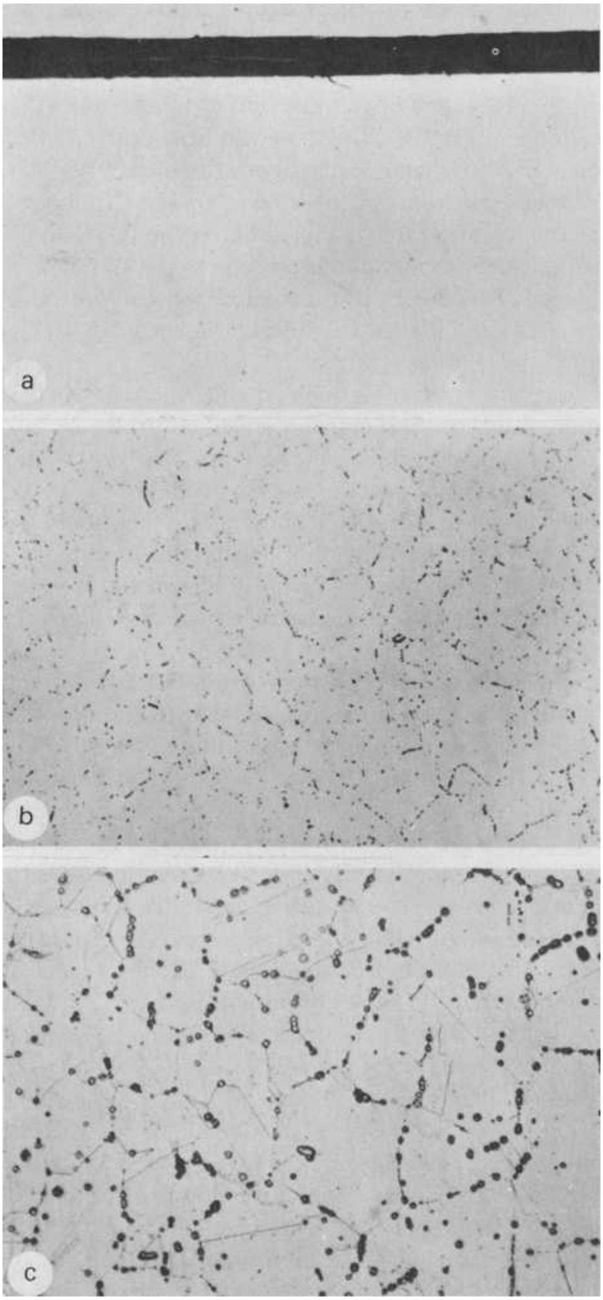

FIG. 7—*Etch structures in Type 304 stainless steel seamless pipe (Heat TH6656) sensitized 24 h at 500°C and tested for degree of sensitization using three techniques:* (a) *A 262, Practice E (0.2 to 0.8 mil penetration),* ×*187,* (b) *EPR* (P_a = *6.5 C/cm²*), ×*89,* (c) *A 262, Practice A (14 percent ditching).*

ment quantitatively ranks this heat near the lowest end of the scale of susceptible materials. According to the A 262, Practice A test, Heat TH6656 would be expected to be more susceptible to IGSCC than Heats 812292 or 78500, using only degree of sensitization as a criterion.

An intermediate level of IGSCC susceptibility occurred in a heat of 1-in. forged bar (Heat 812292) dynamically tested after the 500 °C/24 h sensitization treatment. A specimen from this heat revealed IGSCC about 2 to 3 grains deep (Fig. 8) and a transgranular region below the IGSCC initiated cracks. The sensitization measurement etch structures for this heat are shown in Fig. 9. The A 262, Practice E, test indicated penetrations of 0.1 to 0.4 mil, which occurred at slip planes (Fig. 9*a*) produced by surface cold work during specimen machining.

The EPR test gave a relatively high value (P_a = 16.8 C/cm^2) for degree of sensitization, and the structure revealed a profusion of precipitated carbides (Fig. 9*b*). The carbides present are very small and difficult to resolve using conventional metallographic techniques. This precipitation mode probably accounts for the lack of grain boundary grooving after A 262, Practice A, testing (Fig. 9*c*), where the chromium carbides are presumably too small for the sensitivity of the oxalic acid test. Thus, an advantage is shown for the EPR test method, particularly for some precipitate morphologies.

Generally, the A 262 tests (Practices A and E) are not sufficiently discerning to distinguish between degrees of sensitization at these low levels of sensitization. One exception is the evaluation of the 66-cm (26-in.) rolled and welded pipe (Heat 834264), which has exhibited inconsistent behavior in other related studies [*6*]. Specimens from this large-grained (ASTM 3.5 compared to 5 to 5.5 for the other materials) material are highly susceptible to IGSCC but consistently yield relatively low sensitization values in the EPR test. The A 262, Practice E, test also indicates relatively low levels of sensitization, but the A 262, Practice A, test ranked this heat properly. Although the EPR technique gave a low P_a value for this heat, the post-test appearance did show considerable grooving of the grain boundaries, indicating that post-test examination of the EPR attack should be weighted in the decision process at low P_a values.

Analysis of the remainder of the data in Table 4 indicates the EPR test is more sensitive than either A 262, Practices A or E, in distinguishing and quantifying degree of sensitization at these lower levels of sensitization. It is significant that the high IGSCC susceptibility of Heat M7616 can be eliminated by solution annealing, even when the material is subsequently given the low-temperature sensitization treatment. It was difficult to solution anneal this material adequately, however, as even rapid air cooling after the 1038 °C/h anneal resulted in a sensitized structure similar to the mill-annealed condition given in Table 4. Complete solution annealing was accomplished in this heat only after water quenching in the cooling chamber

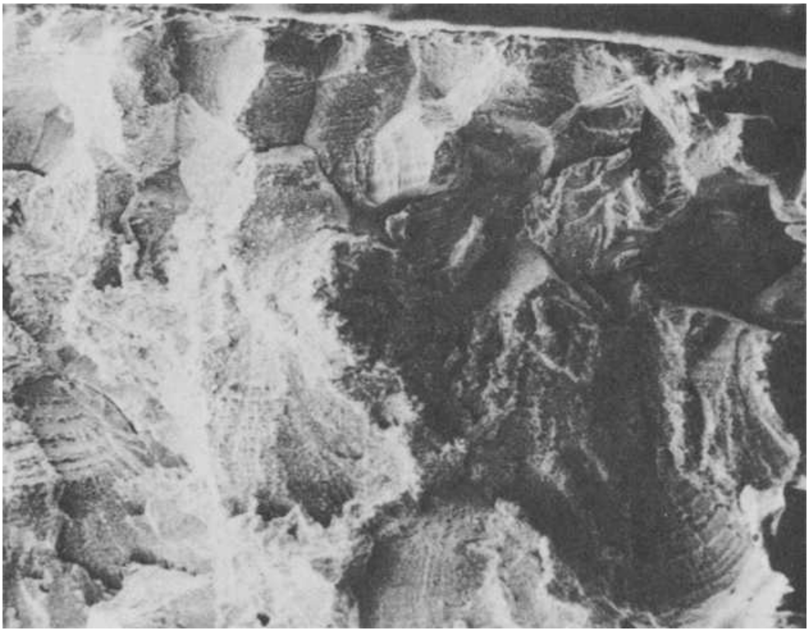

FIG. 8—*IGSCC in sensitized (500°C/24 h) Type 304 stainless steel (Heat 812292) tested by dynamic strain in 289°C water with 8-ppm* O_2 *at extension rate of 0.0008 mm/min.*

of the heat-treat furnace. Apparently, the precipitation of chromium carbides occurs extremely fast during cooling from the solution-annealing temperature, such that a "seeding" effect results which enhances sensitization during subsequent thermal treatments in the sensitization range [*1*].

Additional work was conducted to assess the three measurement methods after more severe sensitization heat treatments. Measurements were performed on a heat of 2.5-cm (1-in.) plate (Heat X14902) which was sensitized 1, 4, 20, and 40 h at 620°C and furnace cooled. These results are given in Table 5, where all three methods indicate a saturation effect for this heat after sensitizing for 20 h or greater. All three methods reveal the lack of sensitization in the as-received condition (mill annealed). The EPR and A 262, Practice A, tests indicate a lower degree for specimens sensitized 4 h compared to 1 h, but this trend could be due to specimen variability, since the A 262, Practice E, tests were conducted on separate specimens while the A 262, Practice A, and EPR tests were conducted on the same specimens. All these sensitized specimens were susceptible to IGSCC after constant load testing in the severe environment of 289°C water with 8-ppm dissolved oxygen [*6*].

Six of the seamless pipe heats were evaluated further after sensitizing for 40 h at 620°C and furnace cooled. This sensitization treatment caused extensive IGSCC susceptibility in all the Type 304 stainless steel pipe spec-

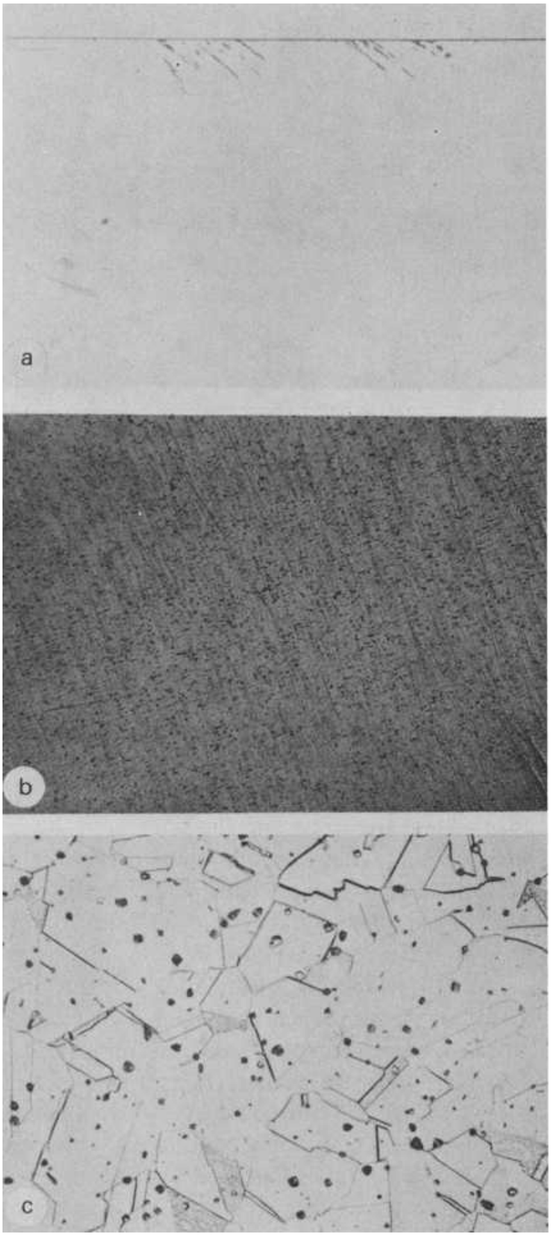

FIG. 9—*Etch structures in Type 304 stainless steel forged bar (Heat 812292) sensitized 24 h at 500°C and tested for degree of sensitization using three techniques:* (a) *A 262, Practice E (0.1 to 0.4 mil penetration), ×175,* (b) *EPR* ($P_a = 16.8$ C/cm^2), (c) *A 262, Practice A* (≤ *1 percent ditching), ×175.*

TABLE 5—*Comparison of A 262, Practices A and E, with the EPR method for measuring degree of sensitization in Type 304 plate (Heat X14902).*

Time at 620°C (1150°F) (h)	Average Penetration Rate mm/h (mil/h)	EPR Measurement P_a (C/cm^2)	Practice A (% Ditching)
As Received	0.00015 (0.006)	$< 10^{-3}$	≤ 1
1	0.0088 (0.345)	14.4	25 to 35
4	0.0232 (0.915)	11.1	3 to 5
20	0.0478 (1.88)	38.4	100
40	0.0432 (1.70)	39.5	100

imens tested by dynamic strain or constant load in the highly aggressive 289°C water with 8-ppm oxygen [*6*]. A typical example is shown in Fig. 10 for Heat M7616 tested by dynamic strain. These results (Table 6) indicate that the A 262, Practice E, test is the most discriminating for greater degrees of sensitization. Both the EPR and A 262, Practice A, tests reflect a "saturation" effect (Fig. 11), where any additional sensitization is not

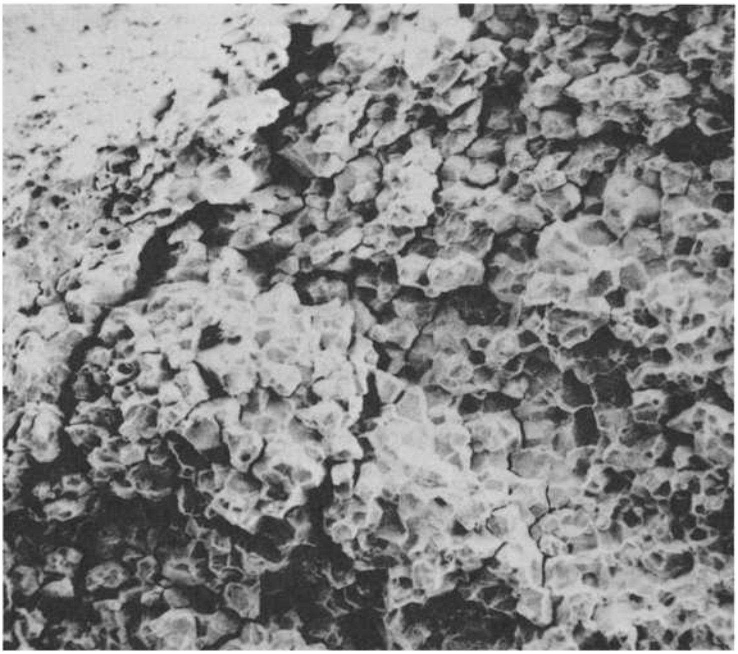

FIG. 10—*Fracture surface of furnace-sensitized (620°C/40 h) Type 304 stainless steel (Heat M7616) tested by dynamic strain in 289°C water with 8-ppm O_2 at extension rate of 0.0008 mm/min.*

TABLE 6—*Comparison of three methods for measuring degree of sensitization of six IGSCC susceptible heats of Type 304 stainless steel seamless pipe sensitized 40 h at 620°C (1150°F).*

Heat	A262-A (% Ditching)	A262-E mm/h (mil/h)	EPR, P_a (C/cm^2)
M7616	100	0.057 (2.23)	120
M7772	100	0.028 (1.11)	85
2P6424	100	0.017 (0.65)	77
2P6396	100	0.010 (0.40)	79
454659	100	0.002 (0.08)	100
TH6656	100	0.0005 (0.02)	85

distinguished by the test. The A 262, Practice A, test reveals a 100 percent ditched structure for all heats given a severe sensitization treatment. The EPR test produces very high P_a values but not a great deal of difference on a heat-to-heat basis, compared to that measured for the lower levels of sensitization.

In contrast to this, the quantified A 262, Practice E, test does appear to distinguish between heats given severe sensitization heat treatments since it is measuring a penetration mechanism, rather than a surface effect where a response is limited to the width of the affected grain boundaries.

Discussion

The three test methods evaluated measure degree of sensitization in somewhat different manners [2]. The EPR method measures the current flow associated with active dissolution of chromium-depleted grain boundary areas as the potential is swept through the active range at a fixed rate. The A 262, Practice A, test evaluates the degree of grain boundary "ditching," presumably as a result of dissolution of grain boundary chromium carbides. Finally, the A 262, Practice E, test considers the extent of grain boundary attack which occurs in chromium-depleted areas in an aggressive corrodent at a fixed potential set by the solution. Each method has a set of "boundary" conditions within which it is capable of discriminating between different degrees of sensitization.

The upper boundary limit of the EPR test is the current associated with complete grain boundary activation. Once this condition is reached, the test will not be sensitive to higher degrees of chromium depletion. The lower limit is established by the sensitivity of the electronic circuitry for detection of current flow through the specimen.

The upper limit for A 262, Practice A, is 100 percent grain boundary ditching, after which no further discriminations between more severely

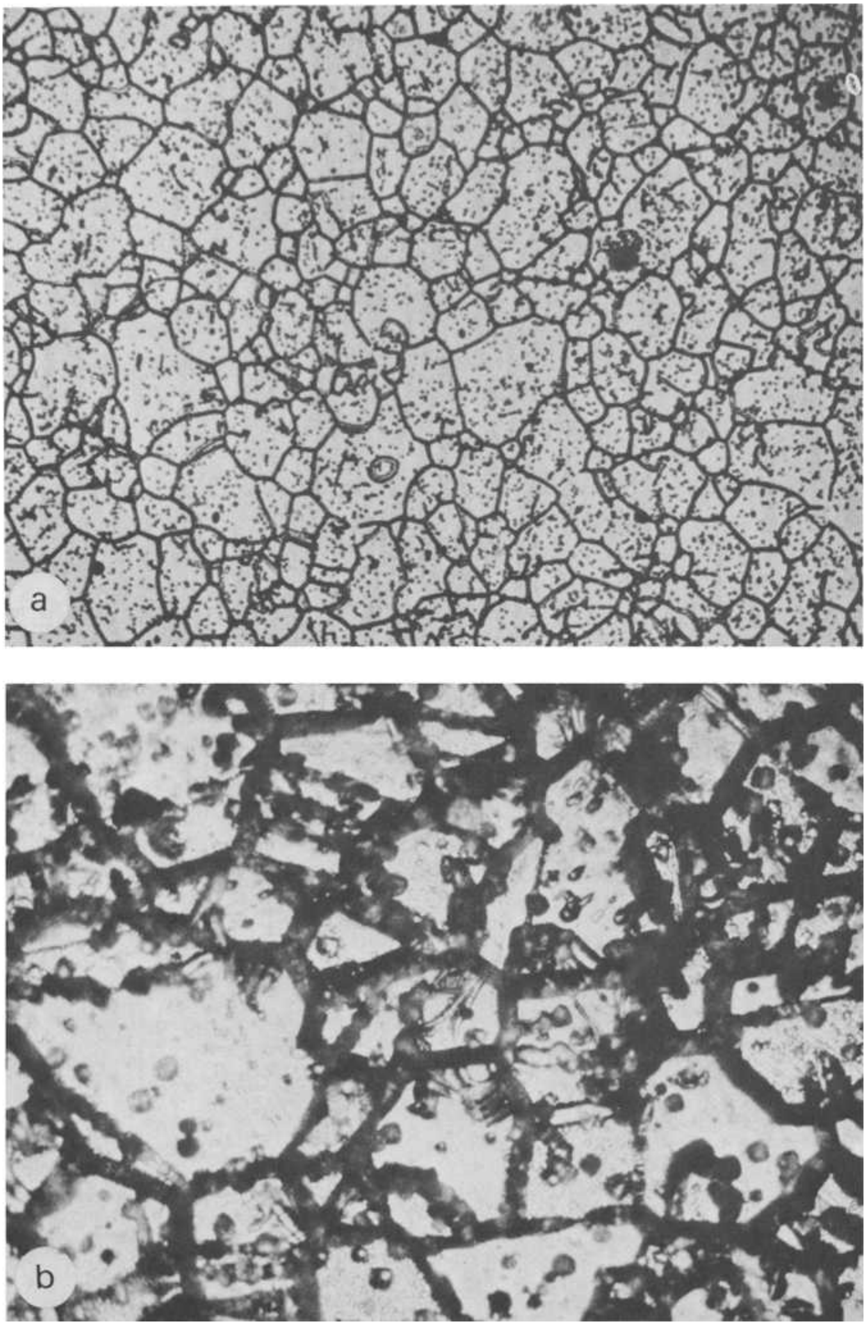

FIG. 11—*Furnace-sensitized (620°C/40 h) Type 304 stainless steel (Heat M7616) showing etch structures* (a) *after EPR testing, ×118,* (b) *after A 262, Practice A testing, ×200.*

sensitized materials can be made. No nationally recognized lower limit has been established for this test; below some degree of sensitization, no discriminations can be made because no grain boundary ditching is observed. It must be pointed up, however, that, according to ASTM procedures, it is not the objective of the A 262, Practice A, test to give quantitative data, but to provide qualitative results on a "go/no go" basis.

In the quantified A 262, Practice E, test there probably exists some upper limit of sensitization detection which is reaction rate limited, that is, the corrodent cannot reach the susceptible grain boundaries at a sufficiently rapid rate. However, this upper limit has not been observed in our tests to date. In the conventional A 262, Practice E, test, the upper limit is the observance of some degree of fissuring and would probably vary from one individual evaluation to another [*4*]. The lower limit for the quantified A 262, Practice E, test appears to be a penetration of about 5.0×10^{-4} cm (0.0002 in.). The exposure time required to achieve this depth of attack will vary with the degree of sensitization of the material (low levels of sensitization such as encountered in welding usually require at least three 72-h exposures). In the conventional A 262, Practice E, method, the lower limit is the lack of observance of "fissuring."

Given these characteristics of the three tests, one would expect the EPR test to be the most discriminating over the full range of degrees of sensitization and certainly the most useful for the levels of sensitization which are of principal concern to the industry. Although it is true the EPR test saturates out compared to the A 262, Practice E, method at higher degrees of sensitization (Fig. 12), these higher degrees are not of practical importance to the industry. The primary concerns relative to sensitization in Type 304 stainless steels are the low levels encountered during production and fabrication (for example, welding and heat treating). It is at these low levels of sensitization that the A 262, Practice E, test loses its discriminating power. Additionally, because of its limited range of detection, the A 262,

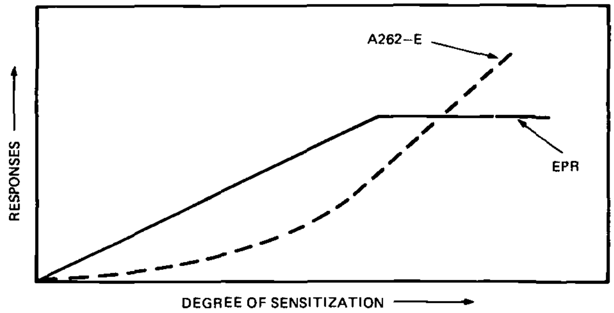

FIG. 12—*Conceptual schematic of relative test behavior.*

Practice A, test would be the least discriminating of the three methods over the full range of sensitization, and this hypothesis is supported by the results of this study and other performed at the General Electric Company [4].

A further advantage of the EPR technique is that it appears capable of providing "go/no go" indications of relative IGSCC susceptibilities for multiple heats of Type 304 stainless steel in moderately sensitized conditions. For example, a plot of I_{DS} versus EPR determined degree of sensitization (P_a) for eleven of the twelve heats studied is shown in Fig. 13. Here, a least squares fit of the data provides a correlation coefficient of

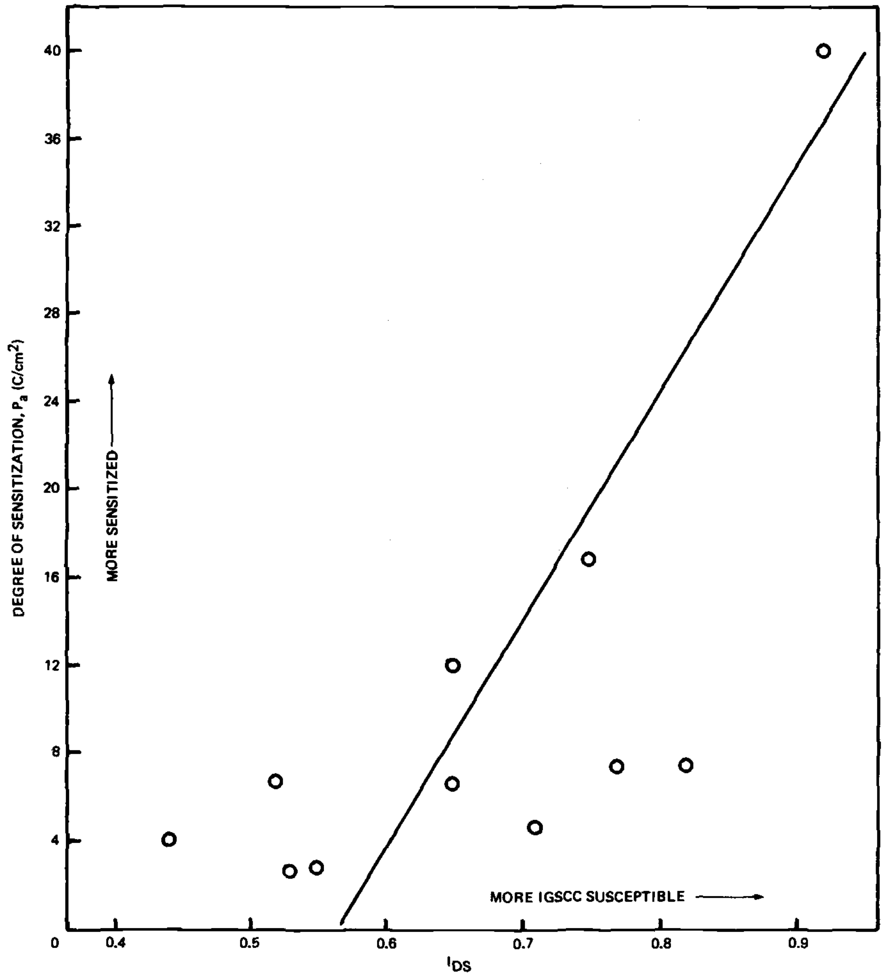

FIG. 13—*Correlation between degree of sensitization and IGSCC resistance for eleven heats of Type 304 stainless steel sensitized 24 h at 500°C (correlation coefficient,* r, *= 0.70).*

0.70, which indicates a good agreement between IGSCC in the extremely severe test used in this study and degree of sensitization after a moderate sensitization treatment. An even better correlation in this extremely aggressive environment is obtained by performing a similar analysis, but using welded specimens of the ten piping heats, where the degree of sensitization is slightly higher [*5*]. As shown in Fig. 14, the correlation coefficient here is 0.89, which significantly supports the potential of the EPR method for detecting IGSCC in sensitized stainless steel. Finally, work being conducted under U.S. Nuclear Regulatory Commission sponsorship [*6*] indicates that the EPR technique may be adapted for quantitative measurement of degree of sensitization in the field nondestructively, which is not possible using either of the other two measurement techniques.

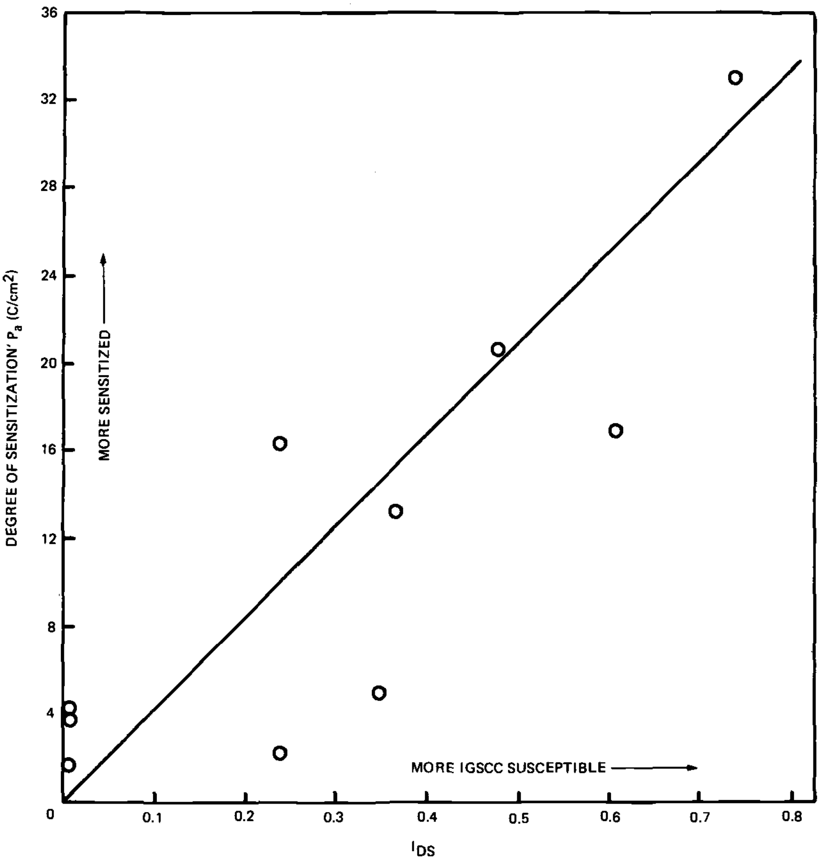

FIG. 14—*Correlation between degree of sensitization determined by EPR and IGSCC resistance for ten heats of Type 304 stainless steel in as-welded condition (correlation coefficient,* r, = *0.89).*

Conclusion

Based on the results of this study, the following conclusions can be made:

1. The EPR method is considered the most sensitive for quantitatively measuring the levels of sensitization which are of primary concern to the industry.
2. All three methods are capable of detecting moderate-to-severe degrees of sensitization in austenitic stainless steel.
3. Both the EPR and the A 262, Practice A, method appear to saturate at the higher degree of sensitization, which results in a loss of discriminating power between different heats of material.
4. The A 262, Practice E, test does not saturate, and retains its discriminating power at high degrees of sensitization, but it is not a suitable method for detection at the lower degrees of sensitization.
5. The EPR method is the most suitable for detecting potential susceptibility to IGSCC and is the only technique considered adaptable for obtaining quantitative information in the field nondestructively. For use in industry, this method will be required to correlate the EPR method to the industrial environment of concern if it is to be used as an indication of IGSCC potential rather than as a measure of sensitization caused by grain boundary chromium depletion.

Acknowledgments

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APPENDIX I

Determination of Carbide Precipitation in Wrought Austenitic Stainless Steels

Scope

This document describes a method for determining the relative amounts of carbide precipitation in the grain boundaries of wrought Types 304, 304L, 316, and 316L austenitic stainless steel used in this study.

Applicable Documents, Codes, and Standards

Codes and Standards—The following codes and standards form a part of this specification to the extent specified herein.

American Society for Testing and Materials—(*a*) ASTM A 262, and (*b*) ASTM, Estimating an Average Grain Size of Metals (E 112-74).

Examination Requirements

The material shall be evaluated in accordance with ASTM A 262, Practice A, as modified by this specification. The low-carbon grades, Types 304L and 316L, shall be heat treated (sensitized) at 1250°F for 1 h before testing.

The evaluation shall include a relationship between the length of the ditched grain boundaries and the total length of the grain boundaries, expressed as percentage, from a representative photomicrograph. The procedure shall consist of determining the ASTM grain size number per ASTM E 112. A representative photomicrograph at an appropriate magnification shall be prepared based on the following table and the portion of the grain boundaries that are ditched shall be crosshatched to facilitate measurement and calculation of relative percentage of ditched to total grain boundary (twin boundaries excluded).

Range of ASTM Grain Size Numbers	Photomicrograph Magnification
0 to 4.5	100
5.0 to 5.5	200
6.0 to 7.5	400
8.00 to 10	500

Method—The following illustrates the method to be used in the evaluation. The relative percentages of ditched grain boundary length versus the total grain boundary length are determined as follows. An overlay is made of the total grain boundary structure.

The differentiation between grain and twin boundaries from photomicrographs can be difficult, especially at the lower percentages of ditching. The simultaneous use of the photomicrograph and the same area viewed through the microscope may be necessary to distinguish between the grain and twin boundaries. Also, a second etching step may be used to delineate the grain boundaries. The second etching procedure consists of electrolytic 60 percent nitric acid (HNO_3) at 40 mA/cm^2 and an etching time of 30 s. The time can be increased depending on the individual specimen requirements.

An alternate method for developing an overlay of the total grain boundary structure is to take a second specimen of material in close proximity and representing the same cross section and grain size. Grain boundary enhancement may be accomplished by either (*a*) sensitizing the specimen at 649 to 670°C (1200 to 1250°F), mounting, polishing, and etching with electrolytic oxalic acid, or (*b*) mounting, polishing, and etching with electrolytic HNO_3 per the previous paragraph. The total grain boundary length may be taken from this overlay per the previous paragraph.

The portion of the total grain boundaries that are ditched should be identified on the overlay. Discontinuous globular carbides are excluded from consideration as ditches.

The lengths of the total and ditched grain boundaries can be measured using an instrument, such as a Dietzgen "Plan Measure," Model 1719B, and the relative percentage of ditched to total calculated.

Specimen Configuration—The full cross section of material 2.5 cm (1 in.) thick or less shall be mounted to provide good edge retention. Thicker specimens may be cut and mounted separately so that the full cross section is examined.

Quality Assurance Provisions

Sampling—Unless otherwise approved in an engineering-approved quality plan, at least one test specimen per each heat-treat lot shall be tested. If the heat-treat lot contains material from more than one mill heat, a separate specimen from each mill heat shall be tested. Forgings, pipe, and other product forms shall be obtained with sufficient additional material to make test specimens.

Certificate of Test—For vendor-supplied material, a statement of test results shall be included in the material test certificate which accompanies the material or shipment and shall include the measured percentage of ditched grain boundary. In addition, a photomicrograph used for the evaluation properly marked with the heat number and heat-treat lot number shall be provided.

APPENDIX II

Quantitative Measurement of General Intergranular Corrosion Susceptibility

Scope

This standard establishes a method for the quantitative determination of the susceptibility of metals to general intergranular corrosion in aggressive chemical environments.

This test method is intended to standardize laboratory test procedures and to provide a means of quantifying the susceptibility of both homogeneously heat-treated materials and materials with localized areas of differential sensitization (such as weld heat-affected zones) to intergranular corrosion.

The method described here is directed primarily toward austenitic alloys which sensitize by carbide precipitation and associated chromium depletion of the grain boundary material. However, the general method may be used with any metal or alloy in any condition by selection of the appropriate test solution.

Summary of Method

This method represents a modification of ASTM A 262, Practice E. The ultimate tensile strength of the material of interest in the desired heat-treat condition is determined and compared with the apparent ultimate tensile strength of corrosion-tested material. The difference between these two values is used to calculate the corrosion which occurred during the test period. The accuracy of measurement of specimen gage section dimensions and failure load becomes increasingly important as the corrosion rate decreases. As described here, the method results in a mean corrosion rate from homogeneously heat-treated material and a mean corrosion rate for the area of maximum sensitization in material with locally sensitized areas. If differential sensitization exists through the test specimen thickness, the calculated corrosion rate will be spuriously low. The minimum depth of attack which can be reliably detected by this method is approximately 5.08 × 10^{-4} cm (0.0002 in.).

The use of the difference in ultimate tensile strength for the calculation of corrosion rates on as-welded specimens may result in large errors in the measured degree of sensitization in weld heat-affected zone material as a function of the through-wall thickness at which the specimen gage section is located. If degree of sensitization of either crown or root side original surfaces is of interest, then the ultimate tensile strength method is not suitable for such measurements and will result in low values. Under these circumstances, the depth of attack should be measured metallographically and the corrosion rate calculated from the observed depth of attack.

Test Apparatus

The test apparatus shall be in accordance with Section 31 of ASTM A 262.

Test Solution

Unless specified otherwise, the test solution shall be prepared in accordance with Sections 32 and 33 of ASTM A 262. Any appropriate solution may be used with this method to investigate corrosive effects. ASTM A 262, Practice E, solution was selected because of the highly localized nature of the attack on sensitized grain boundaries in the austenitic stainless steels and the relative insensitivity of the solution to the buildup of corrosion products, as contrasted to Practice C solution (65 percent HNO_3).

Specimen Preparation

Careful control of gage cross-sectional area is essential to the accuracy and reproducibility of this test method, particularly when low corrosion rates are anticipated. Unless a specific surface is of interest, a cylindrical gage section specimen is recommended.

The gage cross-sectional area of the specimen should be such that the failure load of an untested specimen is less than 454 kg (1000 lb) to minimize interpolation errors in reading of the failure load. The gage length should be sufficient to encompass the area(s) of interest in a locally sensitized specimen, such as from a welded sample. A gage length of 1.9 to 2.5 cm is sufficient for most specimens. Longer gage lengths may introduce problems in maintaining a uniform gage cross-sectional area because of bowing of the gage section during machining operations.

Machining of the specimen should be conducted in a manner that does not introduce large amounts of cold work, particularly if a subsequent sensitizing heat treatment is to be performed. A rough shaping cut followed by fine finish cuts or by fine grinding is the recommended procedure.

Each specimen shall be individually identified on at least one tab end and recorded on a data sheet.

Specimens shall be free of welding temper films, heat-treat oxides, and all organic materials before corrosion testing. Dry blasting with 240 grit or finer abrasive particles is recommended for removal of oxides. Care should be taken to maintain uniformity of the gage cross-sectional area over the gage length. Ultrasonic cleaning in an appropriate solvent is recommended for removal of organic materials.

Before testing, the width and thickness, or diameter, of the gage section shall be measured at three locations, approximately ¼, ½, ¾ of the gage length. Measurements shall be made to the nearest 2.5×10^{-4} cm and individually recorded on the data sheet. These values shall be averaged and mean cross-sectional area calculated for each individual specimen.

If metallographic measurement is to be used to determine the depth of intergranular attack, the specimen configuration is not critical. The specimen length should be sufficient to permit gripping at least 1.3 cm away from the center line of the weld if pulling in a tensile machine is to be used to open the intergranular attack. If bending is to be used to open the intergranular attack, the specimen length should be such that at least 1.3 cm on either side of the weld centerline is uniformly strained. The specimen width need be no more than 0.6 cm, and the thickness need be no more than 0.3 cm unless so desired for special purposes. Tab ends are not necessary on specimens to be evaluated metallographically. No measurements of specimen dimensions are required, unless specified in the test plan for special purposes.

Specimen Corrosion Testing

The number of specimens to be corrosion tested and the number of noncorrosion-tested baseline specimens may vary, depending upon a number of different factors when the tensile difference method is used.

If no changes in ultimate tensile strength are anticipated as a result of subsequent heat treatment, it is not necessary to include a baseline specimen with each group of corrosion-tested specimens. A minimum of one baseline specimen shall be used for each heat of material, and a minimum of two baseline specimens shall be used for three to five groups from the same heat of material when the tensile difference method is used.

Triplicate specimens shall be tested if the anticipated corrosion rate is less than 1.3×10^{-4} cm/h. If the corrosion rate is unknown, a single specimen check run without a baseline specimen may be performed to estimate the corrosion rate.

Unless specified otherwise, the test solution shall be in accordance with Sections 32 and 33 of ASTM A 262. Test conditions shall be in accordance with Section 35 of ASTM A 262, except as follows:

The maximum exposure time between solution changes shall be 72 h.

Corrosion test times will vary, depending upon the degree of sensitization of the material being tested. The test time must be of sufficient length to detect intergranular attack ($> 5 \times 10^{-4}$ cm) in lightly sensitized material, but not so long as to permit complete intergranular penetration of the reduced gage section in heavily sensitized material. The following times are presented as general guides and are based on the behavior of Type 304 stainless steel specimens with a gage section diameter of 0.25 cm: (*a*) mill-annealed material—three periods of 72 h each, (*b*) as-welded material (normal heat input)—three periods of 72 h each, (*c*) as-welded material (high heat input)—one or two periods of 72 h each, and (*d*) furnace-sensitized material—one period of 8 h.

Specimen Tensile Testing

All tensile difference specimens shall be pulled to failure at room temperature at a crosshead speed of 0.127 to 0.05 cm/min (0.05 to 0.02 in./min). The same crosshead speed shall be used for all specimens in any single set of groups.

If a single baseline specimen is provided for a set of corrosion-tested specimens, the baseline specimen should be pulled first. If more than one baseline specimen is provided for a set, the baseline specimens should be distributed through the set to account for any drift in the tensile machine load cell.

The load cell used for the tests should have the smallest full-scale load range which will accommodate all the specimens to minimize errors in interpolation of failure load. A cell with a full-scale value of 454 kg (1000 lb) is recommended, with specimen gage cross-sectional area adjusted to this limit as described in the second paragraph under the Specimen Preparation heading.

Recorder charts of the load curve for each specimen shall be provided with the failed specimens. Interpolation of the failure load shall be made to the nearest pound. Accurate interpolation is critical when corrosion rates are low.

The failed halves of each specimen shall be taped together securely and identified externally with the specimen number.

All specimens to be evaluated metallographically shall be subjected to 1 to 3 percent strain at room temperature with the surface of interest in tension. Higher strains may lead to tearing of the unattacked material and misleading results. Specimens shall be polished to a depth sufficient to remove edge effects from straining.

Corrosion Rate Calculations

The baseline failure stress shall be calculated for each of the baseline specimens for a common set and averaged to give mean baseline failure stress.

The corrosion rate shall be calculated for each individual corrosion-tested specimen and the mean corrosion rate and standard deviation calculated for each specimen group. This calculation is performed on the basis of the change in apparent failure stress of the corrosion tested specimens as follows

$$\text{corrosion rate} = \frac{r_o - \sqrt{\dfrac{\sigma_F}{\pi^* \sigma_u}}}{\text{exposure hours}}$$

where

r_o = original specimen radius,
σ_F = failure load, and
σ_u = ultimate tensile strength.

On specimens evaluated metallographically, the depth of attack may be measured directly with a calculated eyepiece (Filar) or from photomicrographs of the surface. At least × 100 is recommended, and higher magnifications may be required for shallow attack. The corrosion rate is calculated by dividing the depth of penetration (in centimetres) by the exposure time (in hours). Representative photographic documentation is recommended.

Sample Evaluation

The fractured tensile difference specimens shall be examined visually and optically for indications of unexpected conditions and all such results noted on the data sheet. These include observations, such as nonuniform necking, preferential intergranular attack, failure in the weld rather than the weld heat-affected zone, and failure in the gage shoulder rather than the gage section. In addition, the location and nature of the failure should be compared between specimens from the same set to evaluate the physical consistency of the results.

Location of the maximum depth of penetration, in reference to the weld center line, should be recorded for each specimen. Differences in depth of penetration between the two sides of the heat-affected zone should be noted if present. Differences in depth of penetration between the surface of primary interest and the opposite surface should be noted. Photographic documentation of observed differences is recommended.

APPENDIX III

Electrochemical Potentiokinetic Reactivation (EPR) Method for Determining Degree of Sensitization in Stainless Steels

Scope

This appendix describes an EPR test method for quantitatively determining the degree of sensitization in thermally treated AISI Types 304, 304L, 316, and 316L stainless steels.

Applicable Documents, Codes, and Standards

Codes and Standards—The following codes and standards form a part of this specification to the extent specified herein: (*a*) ASTM E 112-74, (*b*) ASTM Recommended Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements (G 5-72), (*c*) ASTM Recommended Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing (G 3-74), and (*d*) ASTM Preparation of Metallographic Specimens (E 3-62).

Equipment

Standard Polarization Cell—Requirements shall be in accordance with Section 2.1 of ASTM G 5.

Electrode Holder—Requirements shall be in accordance with Section 2.2 of ASTM G 5.

Potentiostat—Requirements shall be in accordance with Section 2.3 of ASTM G 5.

Potential Measuring Instruments—Requirements shall be in accordance with Section 2.4 of ASTM G 5.

Current Measuring Instruments—Requirements shall be in accordance with Section 2.5 of ASTM G 5.

Current Integration Measurement Instruments—An instrument that is capable of integrating the current under the curve developed during reactivation should be used. The instrument should be capable of measuring a current integral (in coulombs) to within an accuracy of 1 percent of the absolute value of a current range between 0.001 and 1000 mA.

Anodic Polarization Circuit—Requirements shall be in accordance with Section 2.6 of ASTM G 5, except the current integration instrument should be inserted in series with the lead between the working electrode and potentiostat.

Electrodes—Working electrodes can be any shaped piece of metal at least 0.32 cm (1/8 in.) in diameter or on a side, by any suitable thickness, which has a stainless steel electrode holder mounting screw spot-welded on the side opposite to where the measurement will be taken and is potted in a suitable innocuous compound such that only one planar surface is exposed to the electrolyte.

Counter Electrodes—Requirements are in accordance with Section 2.7.2 of ASTM G 5.

Calomel Reference Electrode—Requirements are in accordance with Section 2.8 of ASTM G 5.

Standard Experimental Procedures

Test Specimen Preparation—Prepare the surface within 1 h of the experiment or store the prepared specimen in a suitable desiccating cabinet. Wet grind with 240-grit and 400-grit SiC paper, followed by wet polish with 600-grit silicon carbide (SiC) paper until previous coarse scratches are removed, rinse with water, and dry. The specimens should be final polished in two additonal stages with 6 and 1 μm diamond paste or 0.05-μm alumina slurry on a nylon or silk cloth over microcloth prepared polishing wheel per ASTM E 3.

Mount the specimen on the electrode holder as described in Section 2.2.1 of ASTM G 5. Tighten the assembly by holding the upper end of the mounting rod in a vise or clamp while tightening the mounting nut until the gasket is properly compressed.

Clean the specimen just before immersion into the electrolyte by degreasing with a suitable detergent, rinsing in distilled water then alcohol, and air drying.

Prepare 1 litre of 0.5 M H_2SO_4 + 0.01 M potassium thiocyanate (KCNS) from reagent grade chemicals and distilled water (solution can be made up in bulk and stored for one month). Transfer approximately 500 to 600 ml of solution to clean polarization cell.

Bring the temperature of the solution to 30 ± 1°C by immersing the cell in a controlled temperature water bath or by other convenient means.

Place the specimen, platinum auxiliary electrodes, salt bridge probe, and other components in the test cell. Ensure that the salt bridge is filled with the test solution and contains no air bubbles, particularly in the restricted space within the tip region. The levels of the solution in the reference and polarization cells should be the same to avoid siphoning.

Purge the solution before test initiation for about 2 min and continuously during the test with high purity nitrogen gas (99.90 percent minimum) at 150 cm^3/min.

Adjust the salt bridge probe tip so it is an close to the specimen surface as possible, but not touching the sample or mount.

Record the open-circuit (rest) specimen potential, that is, the corrosion potential, after about a 2-min immersion. If the rest potential does not register normal for the class of alloys being evaluated (− 350 to − 450 mV for Type 304 stainless steel), then cathodically charge the specimen at − 600 mV for 2 to 5 min and recheck the rest potential. If the rest potential is still abnormal (usually around − 200 mV), the specimen must be removed from the flask and repolished to eliminate the tarnish film.

Passivation is accomplished by setting the potential to + 200 mV versus standard calomel electrode and holding for 2 min. Complete passivation can be checked by observing the lack of change on the current integrator instrument output.

Reactivation Scan—Start the potential backscan (cathodic direction) using a potentiodynamic sweep rate of 6 V/h (± 5 percent).

Rezero and start the current integrator instrument, recording the current continuously with change in potential.

The recorder automatically plots the anodic polarization data on semilogarithmic paper in accordance with ASTM G 3. It is acceptable for the EPR evaluation to plot with the potential as the abscissa and the current as the ordinate, in opposition to the recommended standard reference plot in ASTM G 3.

Lock reading on current integrator when current is close to the initial corrosion potential and has just reversed polarity. Record this reading as the integrated current value (in coulombs) in data record sheet.

Put all electrochemical polarization equipment on standby and remove E versus $\log i$ plot from recorder for inclusion in data file.

Remove specimen from cell and holder, rinse in distilled water followed by alcohol rinse, then air dry.

Data Acquisition and Analysis

Test parameters should be recorded as follows: EPR Run No., Specimen No., Material, Heat; Surface Condition; Specimen Location; Test Temperature, Sweep Rate; Passivating Potential/Time; Rest Potential. Use the following data record sheet form or equivalent for recording these data.

Test data to be recorded include the charge, Q, in coulombs (integrated current under anodic portion of curve during reactivation) maximum anodic curve peak height in milliamperes, and Flade potential in millivolts (potential at which anodic curve breaks upward during reactivation). Record on data record sheet.

Each potted specimen should be photographed after test (without additional preparation or etching) at suitable magnification to document the microstructures and extent of grain boundary grooving after the EPR test. An additional photomicrograph must be taken at ×100 to measure grain size. If the specimen is not sufficiently etched after the EPR test to delineate the microstructure for grain size determination, then the specimens should be etched with 10 percent oxalic acid, electrolytically as per ASTM A 262, Practice A, and a photomicrograph obtained. Attach photos to data record sheet.

Determine the surface area by measuring all dimensions to the nearest 0.1 mm.

The integral charge value, Q, should be normalized to the grain boundary area (GBA) of each specimen using the relationship

$$P_a(\mathrm{C/cm^2}) = \frac{Q}{\mathrm{GBA}}$$

and

$$Q = \text{charge measured on current integrating instrument (coulombs)},$$
$$\mathrm{GBA} = A_s\,[5.09544 \times 10^{-3} \exp(0.34696\,X)],$$

where

A_s = specimen Area (cm^2) and
X = ASTM grain size at ×100.

Note: Show calculation in data record sheet.

Electrochemical Potentiokinetic Reactivation—Data Record Sheet

1. EPR run number ______________________________
2. Specimen number ______________________________

3. Material and product form ________________________________
4. Material heat number ______________ Heat treat lot no. ______________
5. Specimen location ________________________________
6. Specimen surface area, A_s ____________________ cm^2
7. Inital rest (corrosion) potential ____________________ mV versus saturated calomel electrode (SCE)
8. Test temperature ____________________ °C
9. Passivating potential time ____________________ mV versus SCE/time
10. Sweep rate ____________________ V/h
11. Integrated current, Q, ____________________ coulombs
12. Maximum anodic current ____________________ mA
13. Flade potential ____________________ mV versus SCE
14. Grain size, X ____________________ ASTM grain size
15. Normalized charge per grain boundary area (P_a) calculation

GBA = grain boundary area,
GBA = $A_s[5.09544 \times 10^{-3} \exp. (0.34696X)]$
GBA = ______________

where

A_s = Specimen area in cm^2,
X = ASTM grain size at ×100,
P_a = Q/GBA where Q = integrated current in coulombs, and
P_a – ______________

____

16. Attach:
    1. Micrograph characterizing microstructure and extent of grain boundary grooving.
    2. Separate micrograph, if needed, used to determine grain size.

Date: ______________

Determined by: ____________________

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B. Vyas[1] *and H. S. Isaacs*[1]

Detecting Susceptibility to Intergranular Corrosion of Stainless Steel Weld Heat-Affected Zones

REFERENCE: Vyas, B. and Issacs, H. S., "**Detecting Susceptibility to Intergranular Corrosion of Stainless Steel Weld Heat-Affected Zones,**" *Intergranular Corrosion of Stainless Steels, ASTM STP 656,* R. F. Steigerwald, Ed., American Society for Testing and Materials, 1978, pp. 133–145.

ABSTRACT: A scanning reference electrode technique has been developed to study intergranular corrosion of austenitic stainless steels. The potential variations produced in the electrolyte due to the intergranular corrosion of the sensitized grain boundaries have been measured by scanning a microtip reference electrode across the heat-affected zone adjacent to a weld. The development of a test based on the scanning reference electrode technique for determining the degree of sensitization of stainless steels has been explored. The technique is particularly useful in determining the degree of sensitization and the location of the sensitized grain boundaries adjacent to welds. The effect of material and welding variables on the location and degree of sensitization has been studied. The results have been compared with conventional tests for detecting susceptibility to intergranular corrosion.

KEY WORDS: stainless steels, intergranular corrosion, welds, heat affected zone, sensitizing, electrochemistry

Intergranular corrosion refers to the localized attack of the grain boundary area in certain environments. In many stainless steels, intergranular corrosion is a result of the sensitization of the steel, that is, the formation of chromium carbide precipitates and the resulting chromium-depleted zones at the grain boundaries during the heating of the metal in the temperature range of 500 to 800°C [*1,2*].[2]

Sensitization due to welding is probably the most common cause of intergranular corrosion in Type 304 stainless steel in service. As the weld bead moves across the metal being joined, the parent metal on both sides of the weld is exposed to a complex thermal history. At some distance from

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

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the weld bead, the material will be in a temperature range of 500 to 800°C, long enough to precipitate chromium carbides at the grain boundaries. If the welded piece is exposed subsequently to an aggressive environment, the sensitized area will then corrode and cause a band of intergranular attack parallel to the weld. In real situations, the complex thermal gradient and the resultant sensitized zone are a function of the as-received material, specimen thickness, thermal conductivity of the material, weld pass speed, number of passes, heat input per millimetre (inch), and other welding process parameters.

A variety of corrosion test methods and media, some of which have been incorporated in American Society for Testing and Materials (ASTM) standards, have been developed to detect sensitization in stainless steels. They include the oxalic acid etch test (ASTM A 262, Practice A) and the Strauss test (ASTM A 262, Practice E) (ASTM Recommended Practices for Detecting Intergranular Attack in Stainless Steels (A 262-75)). In both these tests, the grain boundaries are etched and the degree of etching is observed metallographically. These tests can determine whether a material is sensitized, and, in case of welds, they can determine the area of the heat-affected sensitized zones. However, these techniques do not give any quantitative measure of the degree of sensitization.

The susceptibility to intergranular corrosion has also been evaluated electrochemically. In the electrochemical potentiokinetic reactivation (EPR) technique [*3*], polarization curves of the specimen are obtained by a controlled potential sweep from the passive to the active region (reactivation) in a specific electrolyte. The activation charge, that is, the integrated area of the reactivation peak, is used as a criterion for the measurement of the degree of sensitization. The EPR technique has been shown to be a viable method for quantitatively measuring sensitization in furnace-sensitized Type 304 stainless steel. The EPR technique has also been used to measure the degree of sensitization and its location in the heat-affected zones (HAZ) adjacent to the welds by successively machining material away from a cross section of the welded specimen and obtaining the activation charge at each plane as a function of the distance from the weld interface. Although the technique is capable of defining the zone of maximum sensitization, it is destructive and time consuming.

In order to evaluate the susceptibility of stainless steel welds to intergranular corrosion, it is necessary to obtain (*a*) the location of the sensitized zone, and (*b*) a quantitative measure of the degree of sensitization in the HAZ adjacent to the weld. This work describes a rapid test which can accomplish these requirements using the scanning reference electrochemical technique (SRET). The SRET has been used to study the effect of material and welding process variables on the degree of intergranular corrosion.

Experimental Technique

A schematic representation of the SRET, showing the electrochemical cell, auxiliary equipment, and the scanning device is shown in Fig. 1. Detailed descriptions of the technique and its operation have been discussed elsewhere [*4,5*]. Basically a microtip reference electrode scans a plane in the solution adjacent and parallel to the surface of the specimen. As the microtip reference electrode scans the surface, it measures the potential variations set up in the electrolyte by the currents flowing from the local corroding sites. The potential changes are recorded on an *x-y* recorder, and the resultant plot represents the magnitude of the corrosion at the localized regions on the specimen surface.

Two sets of welded specimens were prepared for testing. First, two sheets, 150 by 75 by 3 mm thick of as-received Type 304 stainless steel, were joined by manual shielded arc gas welding for varying amounts of heat input. In order to prevent buckling of the steel sheets during welding, they were clamped on a 50-mm (2-in.) thick steel plate, and backshielding was provided by a continuous flow of argon gas. The joined piece was then machined flat and appropriate specimens (WB1–WB4) cut from it. The second set of specimens (WA1–WA4) were obtained by joining two 254 by 100 by 50 mm-thick plates of Type 304 stainless steel. The welding assembly consisted of two plates cut at a wedge angle of 30 deg. One plate was machined (M) at this angle, while the other plate was plasma burned and ground (B). The specimens were preheated up to 90°C for

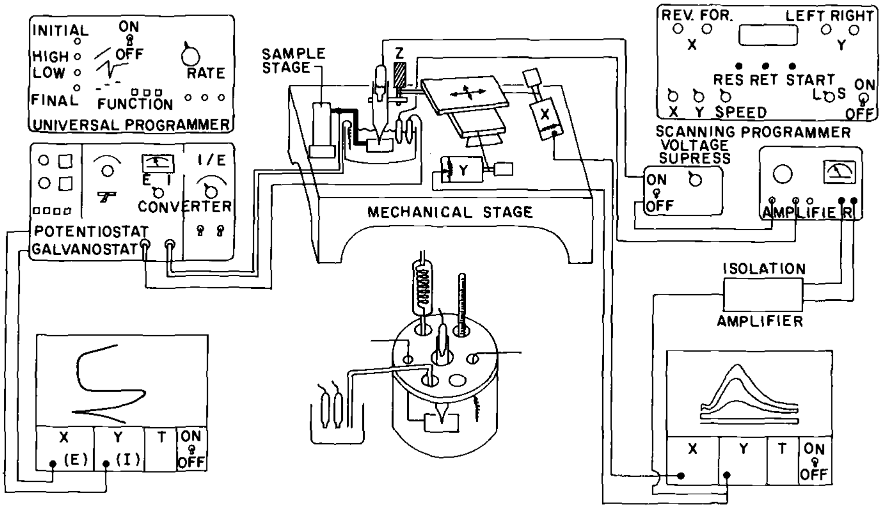

FIG. 1—*Schematic of the scanning reference electrode technique.*

welding, and the interpass temperature was checked at various locations along the weld, both during the welding and at the finish of each bead pass to make sure that the temperature did not exceed 180°C. After welding, the specimens were cut into appropriate specimens and then machine ground flat. The compositions of the steels are given in Table 1.

Specimens were also obtained from a 45.72-cm diameter flange-pipe joint from the primary coolant system of the Brookhaven high flux reactor (HFBR), which had leaked during operation [*6*]. Specimens were taken from two locations on the flange: (*a*) at the bottom of the joint, close to where the intergranular cracks were detected, and (*b*) 120 deg clockwise from the first specimen, where no cracks were observed. All specimens were given a final surface polish of 600 grit before testing.

Electrochemical tests were conducted in an aerated 0.5 *M* sulfuric acid (H_2SO_4) + 0.05 *M* potassium thiocyanate (KCNS) at room temperature, with a platinum auxiliary electrode and a saturated calomel reference electrode against which all potentials were measured. The specimens were held at −500 mV (cathodic potential) for 5 min and then shifted to +200 mV (passive potential). The specimens were allowed to passivate to +200 mV for 2 min and then polarized in the reverse direction potentiokinetically at 3 V/h to −500 mV [*3*]. The reactivated polarization curves obtained by this procedure were recorded on an *x-y* recorder. During the polarization, the microtip reference electrode scanned the surface of the specimen for a distance of 26 mm, from the weld interface across the HAZ into the unaffected base metal, at a speed of 15 mm/min. The distance of the microtip reference electrode from the surface of the specimen was held constant at 100 μm for all experiments. The potential difference between the microtip reference electrode and a stationary reference electrode held close to the unaffected area, away from the weld, was recorded on an *x-y* recorder. The potential difference between the stationary reference electrode and the microtip reference electrode was almost zero over the base metal. As the microtip reference electrode scanned over the sensitized area, a large potential difference incorporating a potential peak was observed. This indicated an accelerated anodic current flowing from the sensitized grain boundaries.

The specimens were examined metallographically after the experiment for verification of the location of the sensitized area. Some of the specimens

TABLE 1—*Chemical composition of Type 304 stainless steel.*

Specimen No.	C	Mn	P	S	Si	Cr	Ni	Fe
WA1-4	0.065	1.41	0.022	0.014	0.53	18.8	9.5	rest
WB1-4	0.07	1.58	0.026	0.007	0.80	18.88	8.61	rest

were also tested by the oxalic acid test and the Strauss test for comparison of the results.

Results

The potential variations measured by the microtip reference electrode as it scanned the weld HAZ, while the specimen was reactivated, are shown in Fig. 2. Also shown in the figure are the polarization curves of the exposed area and a macrograph of the etched area. It is observed that, where the specimen is passive in the potential range of +200 to −100 mV, the potential scans over the weld HAZ are straight lines indicating no preferential attack on the surface. As the surface is reactivated, the potential scan shows a single, defined peak at a fixed distance from the weld interface. This peak increases with an increase in the reactivation current. During reactivation, the sensitized grain boundaries are attacked, that is, an accelerated anodic current flows from these boundaries, and this gives rise to a potential change in the electrolyte, over the corroding area. The macrograph of the attacked specimen confirms that the potential peak occurred over the etched area.

The shape of the broad peak over the sensitized zone in Fig. 2 gives an indication of the variation in intensity of the sensitization in the HAZ. For a distance of up to 1.3 mm away from the weld interface, the potential is

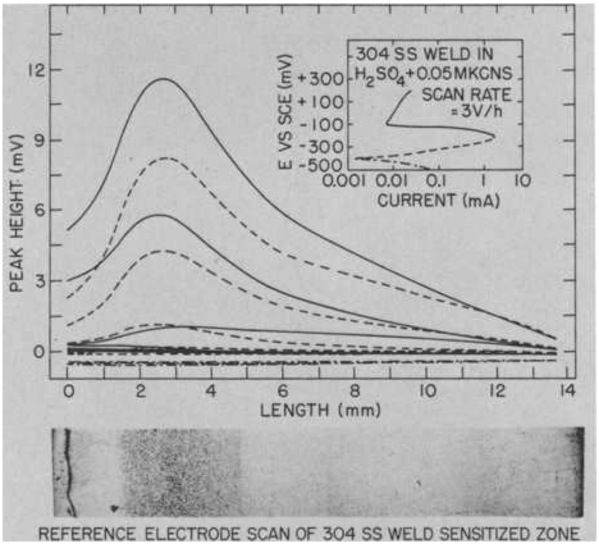

FIG. 2—*Potential changes produced by intergranular corrosion of the sensitized zone adjacent to the Type 304 stainless steel weld in 0.5* M *H_2SO_4 + 0.05* M *KCNS. Also shown are the micrograph of the etched boundaries and the polarization curve of the specimen by the reactivation polarization.*

low. At 1.3 mm, the potential increases sharply, reaching a maximum at 2.5 mm, and then decreases gradually at greater distances from the weld interface. This position and shape of the potential peak correlates well with the degree of etching observed in the photomicrograph. Up to a distance of 1.3 mm, there is no grain boundary etching. At 1.3 mm, a large number of grain boundaries are etched, and the number of etched boundaries increase up to 2.5 mm. Around 2.5 mm, all the grain boundaries are deeply etched. As one moved away, the number of etched grain boundaries decreases, and, further away at ~4.5 mm, only a few grain boundaries are partially etched. Therefore, the magnitude of the potential away from the weld gives a good indication of intensity of sensitization at each point.

A demonstration that the potential fields generated in the electrolyte are due to the currents flowing from the sensitized grain boundaries only, is clearly shown from measurements on a coarse grained weld specimen (Fig. 3). A large grain size (grain size ~1 mm) specimen of Type 304

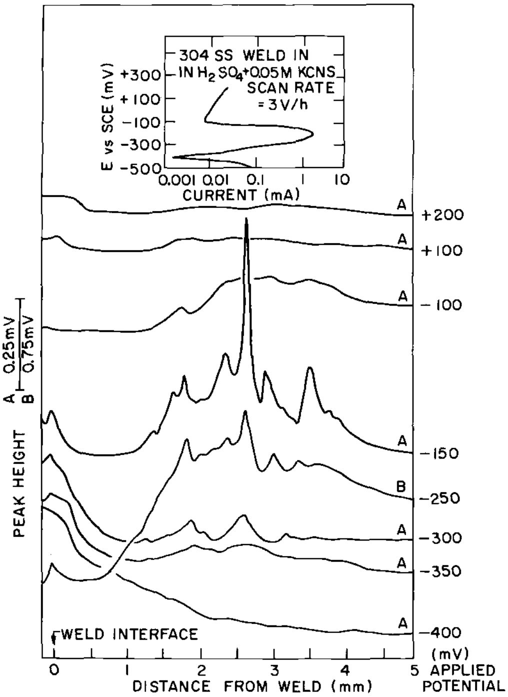

FIG. 3—*Individual potential peaks produced due to intergranular corrosion of the sensitized boundaries in the weld HAZ of a large grain size Type 304 stainless steel specimen at various potentials during reactivation. Also shown is the polarization diagram of the weld specimen during reactivation.*

stainless steel, having the same chemical composition as the WB series given in Table 1, was welded and tested. In this case, as the specimen was reactivated, individual peaks formed in the sensitized zone at a distance of 1.5 to 3.4 mm from the weld interface. On metallographic examination of the specimen, it was observed that the individual peaks correspond to the attacked boundaries in the sensitized zone. No grain boundaries were etched on either side of this sensitized zone, and, correspondingly, no peaks were observed in the potential scan.

The largest potential peak over the HAZ was observed at an applied potential of −200 mV versus saturated calomel electrode (SCE) during reactivation. Therefore, the potential peak at −200 mV was chosen for the comparison of the degree of sensitization produced by different heat inputs and welding procedures.

Potential scans obtained at −200 mV by the reactivation technique for Specimens WB1-WB4 are shown in Fig. 4. The specimens were welded under controlled conditions such that only the heat input of the welding process was varied, all other parameters being kept constant. It is observed that an increase in the heat input increases the magnitude of the degree of sensitization (Fig. 5).

Specimens WA1-WA4, which were welded under shop rather than laboratory conditions, were tested to study the effect of material preparation before welding. Potential scans obtained at the root of the V-notched welds are shown in Fig. 6. It is observed that the material is more sensitized on the side that was prepared by plasma burning (B) than on the machine cut surface (M). Also, the location of maximum sensitization is closer to the weld joint on the (B) side (~2 mm) than on the (M) side (~4 mm).

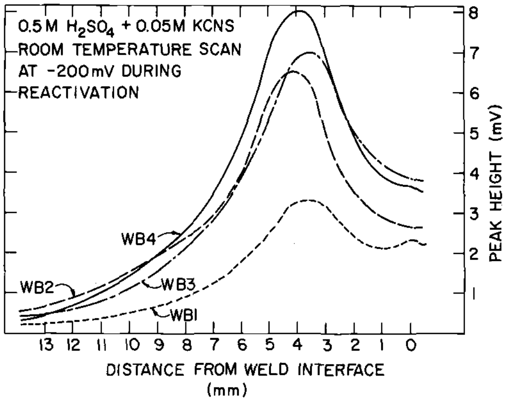

FIG. 4—*Potential scan at −200 mV versus SCE during reactivation of welds WB1-WB4 showing the potential peak over the sensitized zone. WB1-WB4 are welds with increasing heat input during welding.*

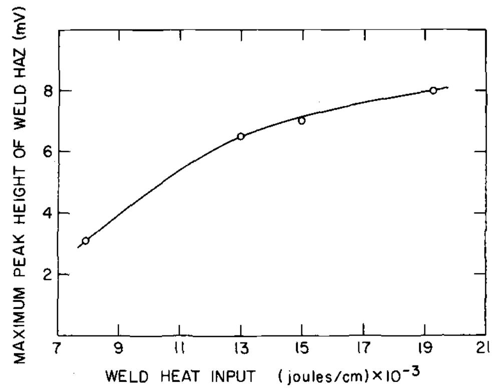

FIG. 5—*Maximum peak height of the potential profile, that is, maximum sensitization versus the heat input during welding.*

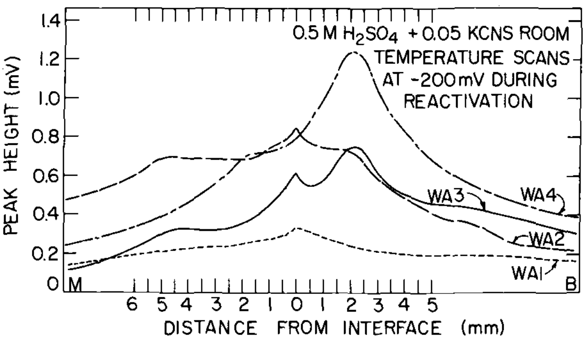

FIG. 6—*Potential scans over the root of the weld specimens WA1-WA4, indicating the potential peaks at −200 mV versus SCE during reactivation. B—plasma burned and ground side of the weld, M—machine cut surface of the weld. WA1-WA4 are specimens with increasing heat input.*

Again in this set of specimens, the degree of sensitization increases with increases in heat input. However, the degree of sensitization is much less than that observed in the WB specimens.

The potential scans for the flange-pipe joint (WC2) at the bottom of the joint (close to where the intergranular crack was detected) and a photomicrograph of the specimen are shown in Fig. 7. It is observed that the flange is sensitized over the entire distance scanned. On further amplifying the potential change over the flange region, a potential peak is observed at a distance of 1.5 to 4.5 mm from the weld interface. On metallographic examination, it is observed that this peak is produced at the cold-worked area of the flange. On the pipe side, very low sensitization is produced in

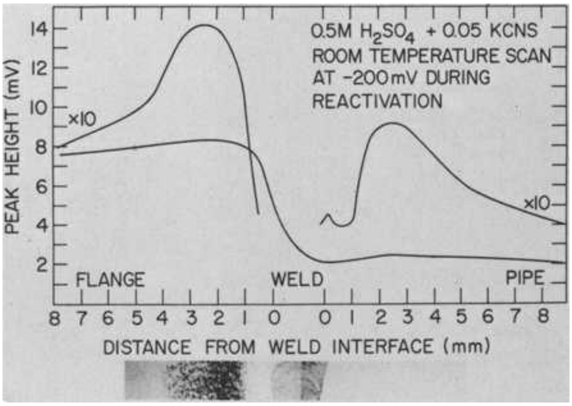

FIG. 7—*Potential profiles over the flange-pipe joint at —200 mV versus SCE during reactivation. The inserts are the magnified* (×*10*) *plots of the lower curve.*

the weld HAZ. The shape of this sensitized zone is typical of those produced by the welding process.

Discussion

It is generally known that the susceptibility of stainless steel welds to intergranular corrosion is localized to a narrow region parallel to the weld bead. There is also a variation in the degree of intergranular attack within the narrow sensitized region. The SRET has been successfully used to give a graphical plot of this variation in susceptibility, as shown in Fig. 2. It can be seen that the magnitude of the potential at each point correlates well with the degree of etching produced in the specimen. The potential scan on the coarse grained weld specimen (Fig. 3) unambiguously illustrates that the potential peaks are generated from the accelerated corrosion current from the sensitized grain boundaries. In the case of fine-grained material, the potential peaks from all the attacked grain boundaries, which cannot be resolved individually, add up to give a single broad peak over the sensitized zone, as shown in Fig. 2.

The effect of increasing the heat input during the welding process is to increase the maximum sensitization in the weld HAZ (Fig. 5). However, for the range of welding heat input used, the location of maximum sensitization and the width of the sensitized zone is not affected appreciably. The maximum in the potential peak, that is, the maximum sensitization, is located ~3.5 to 4.0 mm from the weld interfaces and is comparable to those measured by polishing and measuring the reactivation charge at each point [7]. The half width of the potential peak, which gives an indication of the width of the sensitization, is ~2.5 to 3.5 mm. These observa-

TABLE 2—*Potential changes, maximum anodic current density during reactivation, oxalic acid test, and Strauss test results for the weld specimens.*

Specimen No.	Heat Input, J/in.	Distance from Weld Interface		Maximum Potential Peak Over Weld HAZ, mV	Maximum Current Density, $\mu A/cm^2$	Oxalic Acid Test	Strauss Test	Remarks
		Maximum Potential, mm[a]	Maximum Etching, mm					
WA1	56 942	. . .	. . .	. . .	220	. . .	passed	. . .
WA2	64 338	2.0 (B) 4.2 (M)	1.9 (B) 4.2 (M)	0.72 (B) 0.68 (M)	320	. . .	passed	. . .
WA3	74 800	2.0 (B) 4.5 (M)	2.0 (B) 4.4 (M)	0.77 (B) 0.33 (M)	450	. . .	passed	. . .
WA4	81 600	2.0 (B) 1.5 (M)	2.0 (B) 1.5 (M)	1.25 (B) 0.69 (M)	940	. . .	passed	. . .
WB1	7 800	3.7	3.5	3.3	880	ditch	failed	. . .
WB2	12 937	4.1	4.0	6.5	1 100	ditch	failed	. . .
WB3	14 800	4.2	4.2	6.95	1 400	ditch	failed	. . .
WB4	19 250	3.6	3.6	8.0	2 500	ditch	failed	. . .
WC1 Pipe	medium	2.5	2.5	0.62	300	dual	low attack	. . .
WC1 flange	medium	1 to 9	2 to 6	6.8	12 000	ditch	heavy attack	no cold work, not cracked
WC2 pipe	medium	2.5	2.5	0.78	480	step	low attack	. . .
WC2 flange	medium	1 to 9	2 to 7	7.6	26 000	ditch	heavy attack	cold work, cracked in service

[a] B = plasma burned and ground. M = machined. 1 in. = 25.4 mm.

tions are corroborated by metallographic observation of the specimens after electrochemical testing.

Again in Specimens WA, there is an increase in sensitization with increase in heat input (Table 2). Specimen WA1 (lowest heat input) showed no potential peak; however, on metallographic observation at very high magnification (×800), very slight etching of the grains was observed. It is believed that the potential changes generated are below the detection limit of the technique at the given experimental conditions. However, a very small potential peak could be observed by scanning the microtip reference electrode closer to the specimen surface (20 μm).

Preparation of the metal for welding can change the sensitized zone produced by the welding process, as shown in Fig. 6. The potential peak is higher and located closer to the interface on the plasma burned side than the machine cut side. This change in the location and degree of sensitization resulting from the plasma cutting process can be explained on the basis of the carbide precipitation during welding, as proposed by Tedmon et al [*8*]. The fast quenching following the heating of the metal during the plasma cutting provides a short time at the sensitization temperature to nucleate chromium carbides at the grain boundaries and the subsequent welding heat input causes these carbides to grow. Therefore, the location and degree of the sensitized zone are determined by the plasma cutting process. In general, on the machine cut surface, the sensitized zone was ~4.5 mm away from the interface. However, in the case of Specimen WA4, the sensitized zone is only ~2 mm away from the interface. The results illustrate that the temperature history of metal during welding is extremely complex, and it is not a simple matter to predict the position and the degree of sensitization.

The SRET was used to analyze the inservice failure of the Brookhaven HFBR flange-pipe welded joint. In Specimens WC1 and WC2, the flange was highly sensitized. This sensitization is probably caused by the processing of the flange before welding. On Specimen WC2, taken close to where intergranular stress-corrosion cracking had occurred, a potential peak was generated where the flange was cold worked. The technique, therefore, can also detect structural changes produced in the system which may be a cause of the intergranular cracking. The inservice failure occurred at ~2 mm from the weld interface, that is, at the location of the heavy cold work. The pipe, on the other hand, showed a very small potential peak due to sensitization. Also, the shape of the potential curve was typical of that produced by the welding process (Fig. 7).

Table 2 summarizes the SRET results and the metallographic observations of the various weld specimens studied in this investigation. Also included are the qualitative results from the exposure of these specimens to oxalic acid and the Strauss test according to the ASTM standard procedure. First, the table illustrates the effect of specimen thickness on the degree of sensitization. The degree of sensitization in the WA series (50 mm thick) is less than in the WB series (3 mm thick), although the heat input during welding in the former was greater. The thicker specimens provide a better heat sink and probably dissipate the heat faster away from the weld, resulting in a lower degree of sensitization. However, other factors, such as the weld pass speed and the number of passes, could also contribute to the degree of sensitization, and all these factors have to be considered together to predict the total sensitization produced during welding.

Second, the SRET quantitatively determines the degree and location of the sensitization in all specimens. The SRET measures the degree of sensitization in the WA series which had passed the ASTM Strauss test. Therefore, the technique is more sensitive and superior to the accepted chemical tests. It has been realized that a very low degree of sensitization is enough to cause intergranular stress-corrosion cracking, and, therefore, a more sensitive technique such as the SRET is required to analyze stainless steel welds for their susceptibility to intergranular stress-corrosion cracking.

Conclusion

The SRET is a viable method for measuring sensitization in Type 304 stainless steel welds HAZ and the susceptibility of the weld to intergranular corrosion. The technique gives the location, a quantitative measure, and the variation in the degree of sensitization in the HAZ adjacent to the weld. It is more sensitive than accepted chemical methods of evaluating stainless steel welds. The technique is nondestructive and rapid (each test takes ~15 min), and could be developed into a test for evaluating sensitization in field welds.

The use of the SRET to study the sensitization produced under various material and welding variables has been demonstrated. It has been employed in a failure analysis of specimens from field welds.

The technique seems most promising in evaluating welds for their susceptibility to intergranular stress-corrosion cracking. It is hoped that further work will give a correlation between the location of the sensitized zone and location of the intergranular stress-corrosion cracks. Such a correlation would elucidate the mechanism of intergranular stress-corrosion cracking of sensitized stainless steels.

Acknowledgment

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W. L. Walker[1]

Variations in the Evaluation of ASTM A 262, Practice E, Results (ASTM Subcommittee A01.14 Round Robin)

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ABSTRACT: A total of 42 evaluations in accordance with ASTM Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels (A 262-75), Practice E, were obtained from seven different organizations on the same eleven sensitized Type 304 stainless steel specimens subjected to different exposure times in boiling acidified copper-copper sulfate solution and then bent on a 1-*T* radius. The results indicate that subjective factors influence such evaluations, as evidenced by differences in the classification of the same specimens between different evaluators, with one specimen classified as "passed" and "failed" by approximately equal percentages of evaluators.

KEY WORDS: stainless steels, intergranular corrosion, sensitizing, acidified copper-copper sulfate, evaluation, acceptability, criteria

The acidified copper-copper sulfate test[2-4] for susceptibility to intergranular corrosion of stainless steels was added to ASTM Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels (A 262) as Practice E in 1968 and appeared in the *1970 Annual Book of ASTM Standards* as ASTM A 262-68. Conventionally, it has been used to determine whether the standard carbon grades have been properly solution annealed or if the low-carbon grades were truly resistant to sensitization. More recently, the test has been suggested as a means of evaluating

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[2] Rocha, H. J., *Stahl und Eisen,* Vol. 75, 1955, p. 586.

[3] Scharfstein, L. R. and Eisenbrown, C. M. in *Advances in the Technology of Stainless Steels and Related Alloys, ASTM STP 369,* American Society for Testing and Materials, 1965, pp. 235–239.

[4] Henthorne, M. in *Localized Corrosion—Cause of Metal Failure, ASTM STP 516,* American Society for Testing and Materials, 1972, pp. 66–119.

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the resistance of welded austenitic stainless steels to intergranular stress-corrosion cracking in high-temperature, high-purity water (NRC Regulatory Guide 1.44 "Control of the Use of Sensitized Stainless Steel"). However, the utility of the test for the latter purpose remains to be proven.

The evaluation of Practice E results differs from that of the other four tests of susceptibility to intergranular corrosion contained in ASTM A 262 in that the evaluator is permitted to make a subjective judgment in assigning his rating. In Practice A (electrolytic oxalic acid), the acceptance criterion is defined clearly in terms of the extent of grain boundary ditching. In Practice B (acidified ferric sulfate), the criterion is based on weight loss per unit area, and this same criterion applies to Practice C (nitric acid). In Practice D (nitric-hydrofluoric acid), the criterion is the ratio of two weight loss per unit area values. However, in Practice E, the evaluator is required to decide whether or not "fissuring" is present, without objective criteria for the determination. If this judgment is not made, and the results are classifed as "doubtful," then a metallographic examination is made to determine the "...presence or absence of intergranular attack ...", still without objective criteria against which to base the judgment. Under these circumstances, it is quite possible that the evaluator's expectation or desire regarding the results could influence the evaluation and also possible that the physical equipment used for the examination might influence the results. Examples of both instances have been observed by the writer. In addition, different evaluators may have different individual criteria for their perception of fissuring.

An investigation of the effects of evaluators' expectations and desires on their judgment of Practice E results belongs more properly in a psychological laboratory than in an industrial shop. However, the evaluation of individual subjective criteria appeared to be appropriate for an industrial study. A round-robin test program was initiated by ASTM Subcommittee A01.14 on Methods of Corrosion Testing under Task Group 1418 to determine the extent of variation in evaluations from this source alone.

Procedure

In order to prepare the round-robin specimens, the response of a single heat of Type 304 stainless steel to sensitization at different times at a temperature of 677°C (1250°F) was evaluated by quantified A 262 Practice E, tests. This method was developed by Vermilyea[5] at the General Electric Research and Development Center and modified by the General Electric Boiling Water Reactor Systems Department. Quantification of A 262, Practice E, data is accomplished by carefully measuring the difference between the ultimate tensile strength of a baseline specimen in the condition

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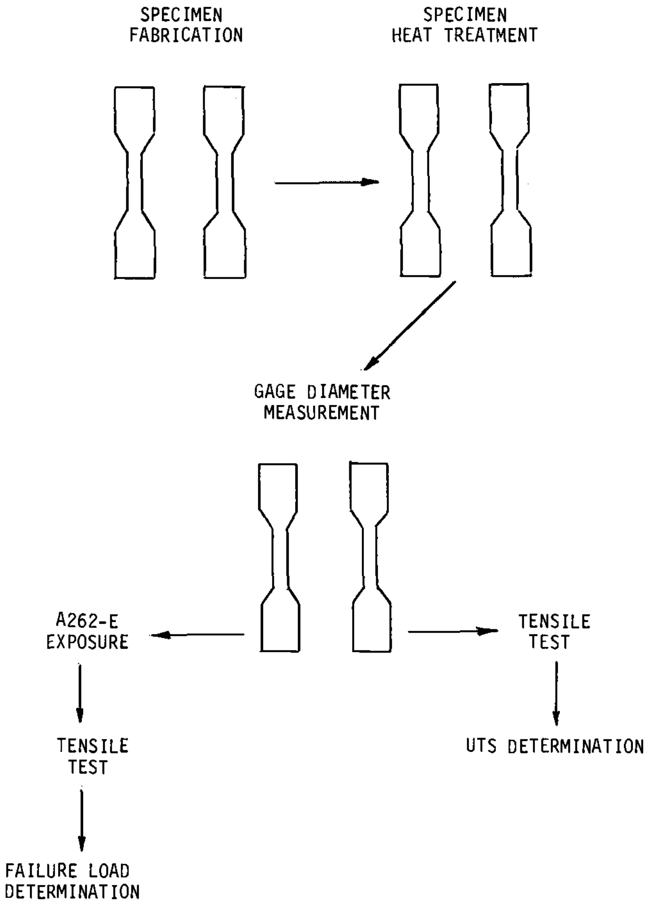
[5] Tedmon, C. S., Jr., Vermilyea, D. A., and Rosolowski, J. H., *Journal of the Electrochemical Society*, 1971, Vol. 118, p. 192.

of interest and the apparent ultimate tensile strength of a specimen which has been exposed to A 262, Practice E, solution for a known period of time. The difference in apparent ultimate tensile strengths of the two specimens can be used to calculate the depth of intergranular attack on the specimen, as shown in Fig. 1. Quantification of the corrosion rate was necessary in order to determine the exposure times required to produce the



$$\text{CORROSION RATE} = \frac{\text{PRE-TEST RADIUS} - \sqrt{\dfrac{\text{FAILURE LOAD}}{\pi \times \text{UTS}}}}{\text{EXPOSURE TIME}}$$

FIG. 1—*Method of quantifying A 262, Practice E, results by apparent difference in ultimate tensile strength.*

round-robin specimens with a range of depths of attack covering the desired range of values. It was determined that a heat treatment of 2 h at 677°C (1250°F) followed by a water quench produced the desired degree of sensitization.

The specimens for the round robin were prepared by cutting transverse sections from a single piece of Type 304 stainless steel bar stock of the composition shown in Table 1. Two half-thickness specimens were then machined from each section. The dimensions of the finished eleven round robin specimens were 7.62 by 1.91 by 0.64 cm (3 by ¾ by ¼ in.). In addition to the rectangular round-robin specimens, cylindrical gage section specimens were also prepared to check the depth of intergranular attack obtained during the A 262, Practice E, exposures by the quantified tensile method. All specimens were solution annealed for 1 h at 1066°C (1950°F) in an inert atmosphere followed by a water quench, and then heat treated for 2 h at 677°C (1250°F) in air, with a water quench. Metal oxides produced during heat-treating were removed from the rectangular round-robin specimens by a 120-grit wet-belt grinder, and from the cylindrical gage specimens by dry blasting with 240-grit silicon carbide.

TABLE 1—*Composition of Type 304 stainless steel used in round-robin study.*

C	Mn	P	S	Si	Cr	Ni
0.042	1.58	0.020	0.011	0.60	18.3	8.9

The length of exposure to A 262, Practice E, solution required to produce the desired depth of attack on each of the round-robin specimens was calculated from the data generated previously using quantified tension specimens. Specimen numbers were assigned to the round-robin specimens from a random number table to prevent the development of a psychological set for increasing depth of attack with increasing specimen numbers by the evaluators. One round-robin specimen was not exposed to A 262, Practice E, solution and acted as a control specimen. The remaining ten round-robin specimens were exposed to A 262, Practice E, solution for time periods of 1.5, 7, 14.25, 21.5, 28.5, 35.75, 43, 50, 57, and 71.5 h. Each round-robin specimen was exposed in a single 1-litre Erlenmeyer flask with ground glass joints and a 4-bulb Allihn condenser, containing 600 ml of A 262, Practice E, solution. In addition to the round-robin specimen, nine of the ten flasks also contained two cyclindrical gage section quantified A 262, Practice E, specimens with individual surface areas of approximately 10 cm^2, giving a minimum solution volume-to-total surface area ratio of approximately 10 ml/cm^2. The bottom of each flask was covered with 50 cm^3 of copper shot.

After exposure, all eleven round-robin specimens were rinsed in demineralized water, dried, and subjected to an ASME Section IX guided bend over a male die with a radius equal to the thickness of the specimens. This was twice the bend radius called for at the time in A 262, Practice E, and was used in order to maximize the area over which fissuring might occur, while still providing severe plastic deformation of the specimen. The round-robin specimens were then cleaned ultrasonically in isopropyl alcohol, dried, and placed in their shipping container in individual compartments to prevent marring of the surfaces. The quantitative A 262, Practice E, specimens were tested to determine if the desired depths of penetration had been achieved. The results indicated fairly good agreement with the predicted depths of attack, except for the specimens exposed at the three longest time periods. In all three cases, the quantitative specimens indicated that the rate of intergranular attack had approximately doubled. No ready explanation for this behavior was apparent.

Representatives of eleven different organizations had volunteered to participate in the round robin and to coordinate the evaluations performed within their respective organizations. A standard set of instructions and rating forms was provided which preceded the specimens to each organization. Evaluations were to be made strictly in accordance with the instructions in A 262, Practice E. A request was made for as many independent evaluations as practical from the organizations, and the importance of the evaluations being completely independent was emphasized. Upon completion of the evaluations by one organization, the round-robin specimens were forwarded to the next participating organization.

The goal of the round robin was to obtain all evaluations and then subject the specimens to destructive metallographic examination to determine the "true" depths of intergranular attack. However, four organizations had not completed their evaluations at the time of presentation of this report during the May 1977 Committee Week, and the partial results were presented without measurement of depths of attack. The results had been quite consistent, and the evaluations obtained had formed a clear pattern. Reducing the total number of evaluations would not appear to have a significant effect on the conclusions of the round robin, and the inclusion of the quantitative data in this publication was considered to be most important. Therefore, the specimens were recalled and subjected to destructive metallographic examination.

Each of the eleven round-robin specimens was sectioned through the specimen midplane and mounted such that at least 1.9 cm (¾ in.) on each side of the apex of the bend was included in the polished area. The specimens were polished and subjected to a light electrolytic oxalic acid etch to delineate grain boundaries. The entire length of the tensile edge of each specimen was examined at a magnification of ×400, and the depth of every intergranular penetration was measured with a Filar reticle and recorded, with the exception of specimen 11. The attack on nine of the ten specimens exposed to A 262, Practice E, solution was "spotty" to varying degrees, with relatively large areas showing no evidence of intergranular attack. On these specimens, individual measurement and recording of penetrations was practical, with the largest number of penetrations (214) observed on Specimen 10. However, Specimen 11 exhibited general intergranular attack, with at least 50 percent of the grain boundaries showing some penetration, and individual measurement and recording of this number was considered to be both impractical and unnecessary. The mean depth of penetration on Specimen 11 was determined by measurements at 55 random locations, made up of two traverses of the full length of the polished bend area. The microscope was defocused, the specimen stage was moved a random distance along the specimen edge, the microscope was refocused, and the depth of attack at the penetration nearest the scale in the reticle was measured. A total of 26 such measurements was made in one of the two traverses, and 29 measurements were made in the other.

Results

A total of 44 different individuals, representing 7 different organizations, evaluated the round-robin specimens. However, one organization submitted a single evaluation report representing the unanimous evaluation of three of its representatives. For purposes of this study, that evaluation was treated as a single evaluation, resulting in a total of 42 evaluations of the specimens. These evaluations are displayed graphically in Fig. 2, with the time of exposure of each specimen to A 262, Practice E, solution and the mean depth of intergranular attack determined by metallographic examination.

Figure 2 clearly shows that there is a wide range of variation between different individuals in their evaluations of the same specimens and that there is a depth of penetration that can be thought of as representing either "maximum confusion" or "minimum discrimination" at approximately 20 μm (0.0008 in.). It would also appear that a mean depth of attack approaching 50 μm (0.002 in.) is required before 95 percent of the evaluators will classify the specimen as "failed." Furthermore, only 88 percent of the evaluators classified the control specimen which saw no exposure to A 262, Practice E, solution as "passed."

The evaluations of Specimens 1 and 2 are anomalous, based on the mean depths of intergranular attack alone. Specimen 1 was exposed to A 262, Practice E, solution for half again as much time as was Specimen 2, yet it exhibited a mean depth of attack less than Specimen 2. However, the quantified tension specimens run with these two specimens gave results consistent with the exposure times, approximately 50 percent greater depth

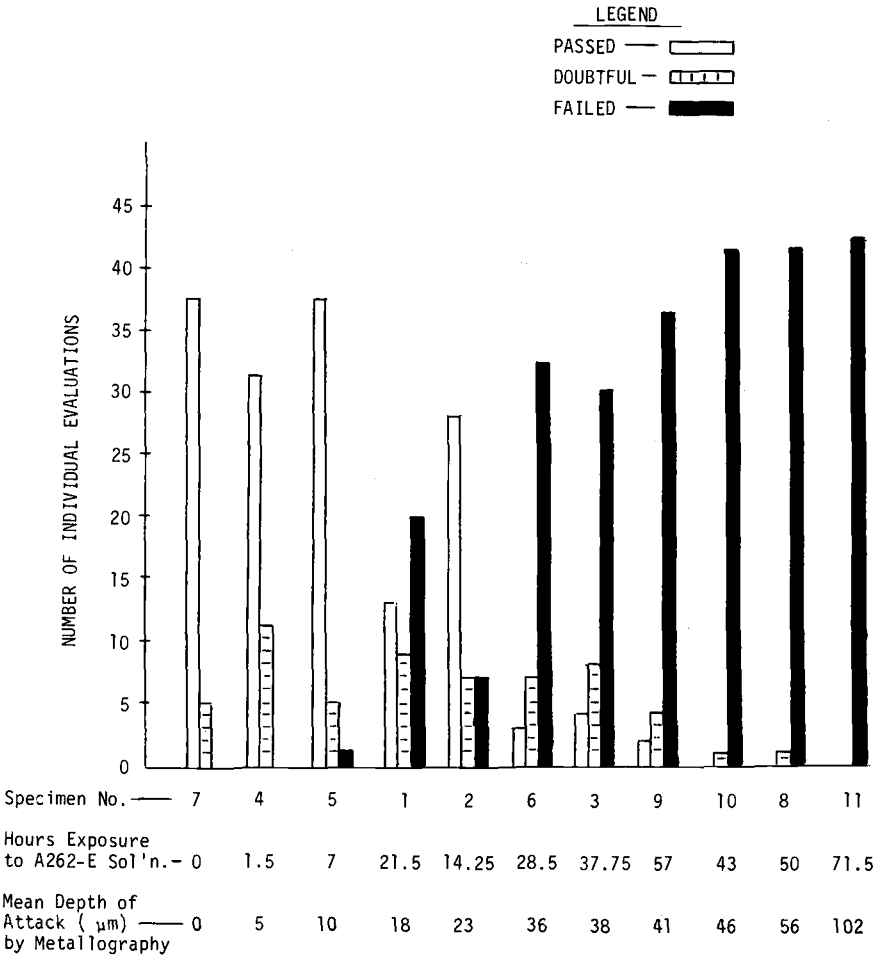


FIG. 2—*Graphical summary of results of 42 individual evaluations of the 11 round-robin specimens.*

of attack on Specimen 1. Furthermore, the evaluators reflect this same expectation, with more evaluators passing—and less evaluators failing—Specimen 2. Examination of the two specimens by scanning electron microscope revealed that the density of intergranular attack on the surface of Specimen 1 was much higher than that observed on Specimen 2, although the mean depth of attack was less. This increased density of attack appears to be the most likely explanation for the anomalous ratings by the evaluators and a specific example of the subjective nature of evaluation of results.

Conclusions

The range of depths of attack over which a particular A 262, Practice E, bend specimen may be either classifed as "passed" or "failed," depending upon the particular individual evaluator, appears to be from 10 to 40 μm (0.0004 to 0.0016 in.). The depth of attack at which one would expect 95 percent of all evaluators to classify such a specimen appears to be near 50 μm (0.002 in.) or greater. There appears to be clear evidence of significant subjective factors exerting an influence on the evalution of A 262, Practice E, bend specimens. Elimination of this factor could be accomplished by instituting metallographic examination of the bend specimens, in conjunction with the specification of some acceptable mean depth of attack as the criterion for acceptance or rejection.

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Niobium and Titanium Requirements for Stabilization of Ferritic Stainless Steels

REFERENCE: Dundas, H. J. and Bond, A. P., "**Niobium and Titanium Requirements for Stabilization of Ferritic Stainless Steels,**" *Intergranular Corrosion of Stainless Alloys ASTM STP* 656, R. F. Steigerwald, Ed., American Society for Testing and Materials, 1978, pp. 154–178.

ABSTRACT: The amount of niobium or titanium necessary to prevent intergranular attack of the weld zone of autogenously welded 18Cr-2Mo and 26Cr-1Mo alloys containing 0.02 to 0.05 percent (C + N) was determined using the copper-copper sulfate ($Cu-CuSO_4$)-16 percent sulfuric acid (H_2SO_4) test. The study demonstrated that a niobium or titanium level equal to or greater than 0.20 percent + 4 (C + N) would produce immunity of 18Cr-2Mo alloys to intergranular attack. The use of the 10 percent oxalic acid etch test and exposure in the 10 percent nitric acid (HNO_3)-3 percent hydrofluoric acid (HF) test, and in a $Cu-CuSO_4$-50 percent H_2SO_4 solution, or an acidified 10 percent ferric chloride ($FeCl_3$) solution confirmed both the effectiveness of the $Cu-CuSO_4$-16 percent H_2SO_4 test and the recommended stabilization formula for alloys containing C + N levels of 0.03 percent. In contrast, the ferric sulfate ($Fe_2(SO_4)_3$)-50 percent H_2SO_4 test produced grain dropping of the weld zone on alloys that were stabilized according to the other tests. Exposure of selected alloys demonstrated that intergranular attack of unstabilized ferritic alloys can also occur in boiling seawater and boiling formic acid.

KEY WORDS: stainless steels, intergranular corrosion, corrosion, ferritic stainless steels, stabilization, pitting, grain boundaries, tests, evaluation

Ferritic stainless steels are attractive because of low alloy cost, excellent resistance to corrosion in many environments, and a high degree of resistance to stress corrosion cracking in hot chlorides. However, because of high diffusion rates of carbon and nitrogen, ferritic alloys may encounter a very rapid intergranular precipitation of chromium carbides and nitrides at temperatures below 925°C (1700°F). The precipitation cannot be prevented even by water quenching. This sensitized condition is frequently produced

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during welding. It is generally accepted that the chromium-enriched compounds readily form at the grain boundaries and produce a chromium-depleted zone which has a lower corrosion resistance than the remainder of the alloy [*1*].[2] The chromium-poor zone, if continuous, is a potential site for intergranular corrosion as well as pitting corrosion. These localized types of attack can have serious consequences that may lead to rapid penetration of the alloys or rapid structural failures. The intergranular precipitation may also seriously reduce the weld ductility and toughness.

Although intergranular corrosion in welded austenitic stainless steels [*2*] is thought to be caused by the same mechanism that causes intergranular corrosion in ferritic stainless steels [*3,4*], the temperatures that produce a sensitization in ferritic alloys are those that eliminate it in austenitic alloys. Furthermore, sensitization of ferritic alloys can occur under a wide range of thermal conditions. Sensitized ferritic alloys are also subject to a lowered corrosion resistance in a wider range of environments than are austenitic alloys. Finally, nitrogen may cause sensitization for ferritic alloys but usually not for austenitic alloys.

Amounts of carbon and nitrogen that are not sufficient to produce sensitization in austenitic alloys will readily produce sensitization in welded ferritic alloys.

Recently developed steelmaking practices make it possible to reduce the carbon and nitrogen content in ferritic stainless steel to levels that prevent damaging precipitation of chromium carbides and nitrides [*5*]. Another means of avoiding sensitization is the use of niobium or titanium to combine with or stabilize the carbon and nitrogen [*6*]. However, the proper use of niobium or titanium stabilization depends upon a prior knowledge of the amount of niobium or titanium necessary to combine with carbon and nitrogen. With current commercial practices, it is possible to obtain C + N levels of about 0.03 percent so that information is needed on the amount of niobium or titanium required to stabilize ferritic alloys of this interstitial content against loss of corrosion resistance.

This investigation was undertaken to determine the amounts of niobium or titanium required to achieve stabilization in autogenously welded ferritic stainless steels. The effect of a heat treatment to simulate the heating effects of welding was also studied. The loss of corrosion resistance resulting from an unstabilized condition was also investigated in chloride-containing solutions and in organic acids.

Materials

This study was performed using experimental alloys for the most part, although some commercially produced, mill-annealed alloys were used.

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

The chemical compositions are given in Table 1. The experimental alloys were produced by induction melting in an argon atmosphere. The resulting ingots were hot forged and hot rolled to 7.6-mm (0.30-in.)-thick strips and then cold rolled to 3.8-mm (0.150-in.) thickness.

The use of different annealing treatments for the niobium-containing alloys was necessary to produce recrystallized structures of similar grain size. The subsequent welding removed all of the effect of variation in annealing treatment from the weld zone and probably most if not all from the heat-affected zone.

The selection of an annealing treatment for the experimental alloys was based on the attainment of a fully recrystallized, fine-grained structure. To achieve this condition, the titanium-containing alloys were annealed at 815°C (1500°F). The niobium-containing alloys were annealed from 815 to 955°C (1500 to 1750°C) depending upon the niobium level. The annealing treatments were of 1-h duration and were followed by a water quench.

Autogenous bead-on-plate welds for corrosion testing were produced on annealed alloys which had been vapor blasted to remove the surface oxide. The gas tungsten-arc process was used to form a molten puddle across one surface of the alloy.

Annealed alloys were also given a heat treatment at 1205°C (2200°F) for 5 min in helium at 75-μm pressure followed by cooling in circulating helium at 1 atm to simulate the heating effects of welding.

Experimental Procedure

Specimen Preparation

Two sizes of specimens were prepared for the corrosion tests: (*a*) 75 by 10 by 2.5 mm (3 by 0.4 by 0.1 in.) for the stress-corrosion tests and for the Cu-copper sulfate ($CuSO_4$)-16 percent sulfuric acid (H_2SO_4) tests, and (*b*) 25 by 20 by 2.5 mm (1 by 0.8 by 0.1 in.) for the remainder of the tests. The specimens were wet surface ground to remove surface irregularities and polished through 600 grit wet metallographic paper. Immediately prior to testing, the specimens were degreased in hot trichlorethylene, washed in a solution of detergent in hot water, rinsed in distilled water, dipped in methanol, dried, and weighed.

Polished 75 by 10 by 2.5 mm (3 by 0.4 by 0.1 in.) strips were bent over an 8-mm (0.32-in.) mandrel to form U-shaped bends that were closed with T304 stainless steel bolts and nuts to provide an elastic strain and were used in stress-corrosion tests. The end portion of the bent specimen was coated with clear varnish to protect the unimmersed portion (bolts and ends of legs).

10 Percent Oxalic Acid Etch Test, ASTM Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels (A 262-A)

The alloy to be studied was mounted in Bakelite and polished through 600 grit wet metallographic paper. The polished cross section of the weld and heat-affected zone was electrolytically etched in a 10 percent solution of oxalic acid at a current density of 1 A per cm^2 for 1.5 min. The welded specimen was the anode, and a stainless steel beaker was made the cathode using a direct current. The etched structures were examined on a metallurgical microscope at ×200 and classified into the following types:

Flat structure
Only slight etching effect with no grooving of grain boundaries.

Dual structure
Some grooving of grain boundaries, but no single grain completely surrounded by grooves.

Groove structure
One or more grains completely surrounded by grooves.

Ferric Sulfate ($Fe_2(SO_4)_3$)-50 Percent H_2SO_4 Test, ASTM A 262-B

The $Fe_2(SO_4)_3$)-50 percent H_2SO_4 test consisted of immersing the specimen for 120 h in individual 1000-ml Erlenmeyer flasks fitted with cold finger condensers and containing 600 ml. of boiling 50 percent sulfuric acid with 25 g of reagent-grade ferric sulfate. The solution level was monitored and the use of the nonstandard cold finger condenser prevented loss of water from the solution.

10 Percent Nitric Acid (HNO_3)-3 Percent Hydrofluoric Acid (HF) Test, ASTM A 262-D

The test was conducted in cylinders of polyvinyl chloride (PVC). The test solution of 10 percent HNO_3-3 percent HF was maintained at 70°C (158°F) with the aid of an oil bath. The exposure was for two 4-h periods with intermediate weighings. The use of 4-h test periods instead of the standard 2 h was intended to increase the severity of the test.

Cu-$CuSO_4$-16 Percent H_2SO_4 Test, ASTM A 262-E

The Cu-$CuSO_4$-16 percent H_2SO_4 tests were performed with the same equipment as that used for the $Fe_2(SO_4)_3$-50 percent H_2SO_4 test. The test

TABLE 1—*Chemical composition.*

	Element, %										Results of Bend Test on Welded Alloys After Exposure to Cu-CuSO$_4$-16% H$_2$SO$_4$
Alloy	Cr	Mo	C	N	Nb	Ti	Si	Mn	S	P	
1	17.61	1.95	0.018	0.004	...[a]	...	...	...	...	...	F[c]
2	18.35	2.02	0.018	0.017	0.10	...	0.48	0.46	0.012	0.020	F
3a	17.75	2.07	0.036	0.031	0.13	...	0.22	0.41	...	...	F
3b	NA[b]	NA	NA	NA	0.32	...	NA	NA	...	...	F
3c	NA	NA	NA	NA	0.61	...	NA	NA	...	...	NF[d]
4	17.8	1.85	0.032	0.021	0.026	...	...	...	...	...	F
5a	17.9	2.05	0.015	0.015	0.19	...	~0.4	~0.5	...	...	NF
5b	NA	NA	0.015	0.015	0.29	...	NA	NA	...	...	NF
6	18.11	2.01	0.017	0.015	0.22	...	~0.4	~0.5	~0.01	~0.015	NF
7	18.2	1.97	0.017	0.016	0.25	...	0.48	0.46	0.013	0.018	NF
8a	17.73	2.01	0.014	0.018	...	...	0.46	0.36	0.009	0.009	F
8b	17.69	2.05	0.014	0.019	0.28	...	NA	NA	NA	NA	NF
8c	17.54	2.02	0.014	0.019	0.57	...	NA	NA	NA	NA	NF
9a	18.20	1.99	0.016	0.013	...	...	0.45	0.36	...	...	F
9b	18.10	2.04	0.019	0.013	0.30	...	NA	NA	NA	NA	NF
10	18.9	2.18	0.015	0.014	0.45	...	0.49	0.44	0.010	0.020	NF
11	18.08	1.95	0.017	0.017	0.52	...	~0.4	~0.5	...	...	NF
12	18.54	1.97	0.035	0.032	0.52	...	0.78	0.91	0.016	0.02	NF
13a	18.08	2.05	0.064	0.028	0.50	...	~0.4	~0.4	~0.015	...	F
13b	NA	NA	NA	NA	0.67	...	NA	NA	NA	...	NF
14a	25.90	1.13	0.009	0.017	0.09	...	...	...	...	...	F
14b	NA	NA	NA	NA	0.17	...	...	...	...	...	F
14c	26.22	1.08	0.015	0.027	0.20	...	...	...	...	...	F
14d	25.98	1.08	0.017	0.027	0.42	...	...	...	...	...	NF
15a	25.60	1.05	0.012	0.013	0.33	...	...	...	...	...	NF
15b	NA	NA	NA	NA	0.44	...	...	...	...	...	NF
15c	NA	NA	NA	NA	0.56	...	...	...	...	...	NF
16	26.37	1.00	0.010	0.027	0.42	...	...	...	...	...	NF

17a	18.53	1.78	0.016	0.011	...	0.09	~0.4	~0.4	...	...	F
17b	NA	NA	0.017	0.010	...	0.15	NA	NA	...	...	F
17c	NA	NA	0.018	0.010	...	0.19	NA	NA	...	...	F
17d	NA	NA	0.018	0.009	...	0.26	NA	NA	...	...	NF
18a	~18.0	~1.8	0.013	0.014	...	0.10	~0.4	~0.4	...	...	F
18b	NA	NA	0.013	0.015	...	0.12	NA	NA	...	...	F
18c	NA	NA	0.014	0.015	...	0.16	NA	NA	...	...	F
19	18.68	1.74	0.015	0.010	...	0.11	0.37	0.42	...	...	F
20a	18.35	1.77	0.013	0.008	...	0.11	~0.4	~0.4	...	...	F
20b	NA	NA	0.014	0.009	...	0.13	NA	NA	...	...	F
20c	NA	NA	0.015	0.007	...	0.16	NA	NA	...	...	F
20d	NA	NA	0.020	0.007	...	0.23	NA	NA	...	...	NF
21	18.95	2.00	0.009	0.010	...	0.17	0.37	0.40	0.007	0.008	NF
22	18.47	1.96	0.015	0.013	...	0.17	~0.4	~0.4	...	...	NF
23	18.49	1.95	0.014	0.013	...	0.24	~0.4	~0.4	...	...	NF
24	18.36	1.92	0.014	0.013	...	0.28	~0.4	~0.4	...	...	NF
25a	17.53	2.04	0.015	0.018	...	0.27	0.45	0.40	0.002	0.009	NF
25b	17.50	2.06	0.014	0.018	...	0.54	NA	NA	NA	NA	NF
26	18.66	2.05	0.017	0.010	...	0.29	0.40	0.35	...	...	NF
27	18.9	2.03	0.018	0.012	...	0.34	0.53	0.45	0.010	0.021	NF
28	18.9	2.05	0.014	0.015	...	0.37	0.49	0.44	0.009	0.022	
29	17.54	2.02	0.015	0.014	...	0.20	0.47	0.40	0.004	0.003	F
30	18.23	1.83	0.025	0.018	...	0.31	...	...	...	...	F
31	18.34	1.90	0.037	0.020	...	0.37	0.28	0.49	...	...	NF
32	18.45	1.97	0.034	0.045	...	0.47	0.13	...	...	...	NF
33	17.94	1.93	0.044	0.052	...	0.42	0.31	0.64	...	...	NF
34	18.0	1.96	0.043	0.057	...	0.45	0.35	0.48	...	...	F
35a	25.53	1.00	0.011	0.015	...	0.17	...	...	...	...	F
35b	NA	NA	NA	NA	...	0.22	...	...	...	...	F
35c	NA	NA	NA	NA	...	0.26	...	...	...	...	NF
35d	26.13	1.10	0.012	0.014	...	0.30	...	...	...	...	NF

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[a] Not added.
[b] In range of series.
[c] Fissuring.
[d] No fissuring.

solution was 500 ml of boiling 16 percent H_2SO_4-6 percent $CuSO_4$. The solution was compounded from distilled water and reagent-grade chemicals. The specimens were suspended in the solution by means of a vented 30-ml beaker that contained 50 g of copper chips. The chips were packed around the specimen to ensure good physical contact. After a 24-h exposure, the specimens were bent over a 1*T* radius through 180 deg, or until failure, with the weld at the apex of the bend. To ensure that any inherent brittleness and resulting cracks would not be misinterpreted as failure due to intergranular corrosion, uncorroded specimens were also bent and examined for cracks.

Cu-$CuSO_4$-50 Percent H_2SO_4 Test

The $CuSO_4$ test utilizing 50 percent H_2SO_4 [7] was performed with the same equipment used for the $Fe_2(SO_4)_3$-50 percent H_2SO_4 test. The test solution consisted of 600 ml of boiling 50 percent H_2SO_4-6 percent $CuSO_4$ solution containing 25 g of copper chips. Contact between the specimen and copper chips was avoided by suspending the specimen in the solution and placing the copper chips on the bottom of the flask. The exposure period was 120 h.

Formic Acid Tests

The boiling acid tests were conducted with the same equipment as that used for the $Fe_2(SO_4)_3$-50 percent H_2SO_4 test. Upon immersion, the specimens were momentarily activated by touching the specimen surface with magnesium. Activation was used to avoid difficulty in interpreting the results. Ferritic stainless steels can exhibit a metastable passive condition in acids.

Pitting Tests

The pitting tests in acidified ferric chloride ($FeCl_3$) were performed in sealed, all-glass vessels with the specimens supported by glass hooks. The solution volume was about 250 ml. The exposure period was 240 h in a water bath at 25°C (77°F).

Stress-Corrosion Cracking Tests

The U-bend specimens were exposed to 600 ml of boiling seawater solution. The tests were carried out in one-litre Erlenmeyer flasks fitted with cold finger condensers. The cracking was determined by visual inspection, and the time for appearance of the cracks was recorded.

The seawater solution was prepared according to ASTM Specification for

Substitute Ocean Water (D 1141-75) by adding 42 g of a commercial sea salt mixture of the following composition to 1 litre of distilled H_2O: sodium chloride (NaCl)—58.49 percent, magnesium chloride ($MgCl_2 \cdot 6H_2O$)—26.49 percent, anhydrous sodium sulfate (Na_2SO_4)—9.75 percent, calcium chloride ($CaCl_2$)—2.77 percent, potassium chloride (KCl)—1.64 percent, sodium bicarbonate ($NaHCO_3$)—0.48 percent, potassium bromide (KBr)—0.24 percent, boric acid (H_3BO_3)—0.071 percent, strontium chloride ($SrCl_2 \cdot 6H_2O$) —0.95 percent, sodium fluoride (NaF)—0.007 percent.

Results

Accelerated Intergranular Corrosion Testing of Autogenous Welds

The results of applying the Cu-$CuSO_4$-16 percent H_2SO_4 test to 18Cr-2Mo and 26Cr-1Mo alloys containing autogenous welds are shown in Figs. 1 and 2 with the niobium or titanium level plotted against the sum of the carbon and nitrogen contents. The alloys contained about equal amounts of carbon and nitrogen, and their effects with regard to intergranular corrosion were assumed to be equal. For completeness, the results are also given in Table 1 along with the composition of the alloys.

The effect of titanium additions on the resistance of welded alloys to intergranular corrosion in the Cu-$CuSo_4$-16 percent H_2SO_4 test is shown in Fig. 1. Titanium additions as low as 0.24 percent completely prevented intergranular corrosion of alloys containing 0.028 percent (C + N). This minimum amount of titanium required is about nine times the combined carbon and nitrogen. Increasing the interstitial level required an increased

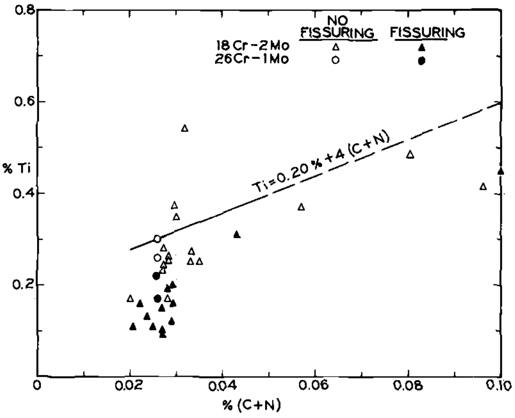


FIG. 1—*Results of bending through 1T radius of autogenously welded 18Cr-2Mo and 26Cr-1Mo alloys containing titanium after exposure to Cu-$CuSO_4$-16 percent H_2SO_4 solution.*

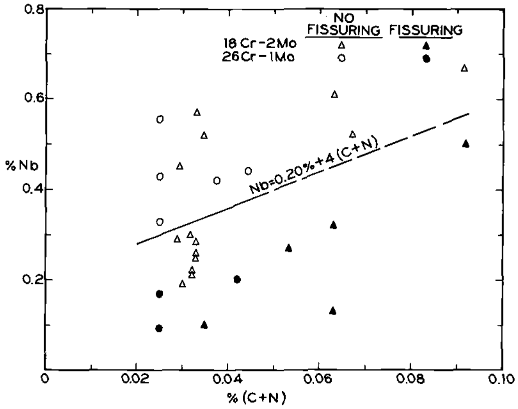


FIG. 2—*Results of bending through 1T radius of autogenously welded 18Cr-2Mo and 26Cr-1Mo alloys containing niobium after exposure to Cu-CuSO$_4$-16 percent H$_2$SO$_4$ solution.*

titanium level to produce stabilization with no evidence of the titanium requirement diminishing significantly up to a C + N level of 0.10 percent. It should be noted that use of a stoichiometric quantity of titanium about 4 (C + N) was not sufficient to prevent intergranular corrosion at any level. A stabilization formula of Ti = 0.20 percent + 4 (C + N) minimum, accepted by ASTM for 18Cr-2Mo alloys containing between 0.020 and 0.050 percent (C + N), is shown in Fig. 1 (ASTM Specification for Heat-Resisting Chromium and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Fusion-Welded Unfired Pressure Vessels (A 240-78). The formula has no theoretical basis, but it was consistent with the results of the 18Cr-2Mo alloys. The margin of safety that was included in the formula is clearly illustrated at C + N levels of 0.020 to 0.030 percent. Although the results of the 26Cr-1Mo alloys containing 0.03 percent (C + N) were in agreement with the formula, there was not a sufficient amount of data at other interstitial levels to allow the use of the formula for alloys other than 18Cr-2Mo.

Autogenous welds in 18Cr-2Mo and 26Cr-1Mo alloys can be stabilized with niobium as well as with titanium as evaluated by the Cu-CuSO$_4$-16 percent H$_2$SO$_4$ test as shown in Fig. 2. However, unlike titanium, the use of a stoichiometric quantity of niobium 7 × (C + N) may provide marginal stabilization, but this would not provide a margin of safety, particularly at the interstitial range of 0.02 to 0.05 percent (C + N). The use of the same formula as for titanium, Nb = 0.20 percent + 4 (C + N) minimum, also has been accepted by the ASTM for 18Cr-2Mo alloys containing from 0.020 to 0.050 percent (C + N) (ASTM Specification A 240-78). The results of the 18Cr-2Mo alloys were in agreement with the formula.

The evaluation of autogenous welds in 18Cr-2Mo alloys containing about

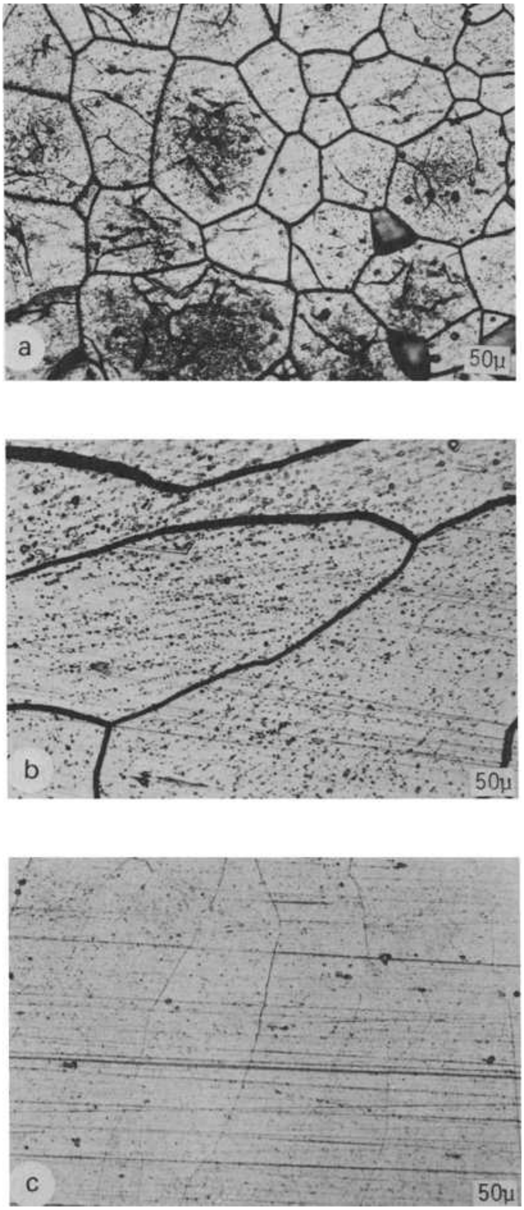
0.03 percent (C + N) using the Cu-CuSO$_4$-16 percent H$_2$SO$_4$ test, the Cu-CuSO$_4$-50 percent H$_2$SO$_4$ test, and the oxalic acid etch test produced similar results, as shown in Table 2, and confirmed the effectiveness of both the Cu-CuSO$_4$-16 percent H$_2$SO$_4$ test and the stabilization formula at this interstitial level. Those alloys that showed signs of fissuring after exposure in Cu-CuSO$_4$-16 percent H$_2$SO$_4$ also encountered grain dropping as a result of intergranular attack in Cu-CuSO$_4$-50 percent H$_2$SO$_4$ and had a grooved microstructure in the oxalic acid etch test. Those alloys that were able to sustain a bend after exposure in Cu-CuSO$_4$-16 percent H$_2$SO$_4$ with no evidence of fissuring also did not encounter grain dropping in Cu-CuSo$_4$-50 percent H$_2$SO$_4$ and had a flat microstructure in the oxalic acid etch test. The corrosion rates in Cu-CuSO$_4$-50 percent H$_2$SO$_4$ are only shown to illustrate the difference in resistance of a stabilized alloy and a greatly understabilized alloy. In this test, the presence of any grain dropping in the weld zone can be considered as an indication of intergranular attack.

The microstructures obtained in the weld area of the 18Cr-2Mo alloys from the oxalic acid etch test are of interest and clearly show the transition from an unstabilized condition to a stabilized condition (Fig. 3). In the absence of titanium, the grain boundaries of the weld zone were heavily etched, producing a grooved structure with some grains being removed. The presence of an insufficient amount of titanium to stabilize the alloy (0.11 percent) also resulted in a grooved structure. The grain boundaries of the weld zone of a stabilized alloy (0.24 percent titanium) were slightly etched and were designated as having a flat surface. It is expected that niobium stabilization also could be successfully evaluated using the oxalic acid etch test. A previous study has shown that this test is not suitable for the detection of a structure susceptible to intergranular corrosion in the T430 (17 Cr-0.049C) and T434 (17Cr-1Mo-0.069C) alloys that contain no titanium or niobium [8]. It is possible that the test would be suitable for T430 and T434 alloys of lower interstitial level.

TABLE 2—*Resistance of autogenously welded 18Cr-2Mo alloys containing about 0.03% (C + N) to intergranular corrosion in various tests.*

Alloy	Ti, %	Cu-CuSO$_4$-16% H$_2$SO$_4$	Cu-CuSO$_4$-50% H$_2$SO$_4$	Microstructure After 10% Oxalic Acid Etch Test
9a	0	fissuring	grain dropping (5989 mdd)[a]	groove
19	0.11	fissuring	grain dropping (1750 mdd)	groove
23	0.24	no fissuring	no grain dropping (72 mdd)	flat
25a	0.27	no fissuring	no grain dropping (82 mdd)	flat
	Nb, %			
9b	0.30	no fissuring	no grain dropping (90 mdd)	flat

[a] Corrosion rate in milligrams per square decimeter per day.



(*a*) 0Ti Alloy 9a, groove structure.
(*b*) 0.11Ti Alloy 19, groove structure.
(*c*) 0.24Ti Alloy 23, flat structure.

FIG. 3—*Microstructure of weld cross section of 18Cr-2Mo-0.03(C + N) alloys containing titanium after exposure to 10 percent oxalic acid etch test.* ×*160.*

Evaluation of the stabilization requirements for autogenously welded 26Cr-1Mo alloys containing about 0.03 percent (C + N) included those tests for the 18Cr-2Mo alloys, as well as the $Fe_2(SO_4)_3$-50 percent H_2SO_4 test and the 10 percent HNO_3-3 percent HF test (Table 3.). The results clearly show that, for stabilization with niobium, all the tests were in agreement. In marked contrast, exposure in $Fe_2(SO_4)_3$-50 percent H_2SO_4 produced grain dropping of the weld zone on titanium-containing alloys that were stabilized according to the other tests and illustrated that this highly oxidizing solution is capable of attacking the alloy in such a way as to produce the appearance of an unstabilized condition. It cannot be determined from these tests whether the intergranular attack of the titanium-stabilized 26Cr-1Mo alloy is a result of attack on the titanium carbonitrides or an invisible sigma phase [*9*]. Of course, intergranular attack of alloys stabilized with titanium in $Fe_2(SO_4)_3$-50 percent H_2SO_4 is not an indication of a general susceptibility to intergranular corrosion. In many situations where highly oxidizing conditions would not be encountered, the proper addition of titanium to ferritic stainless steels would prevent intergranular corrosion of as-welded material. However, titanium-stabilized alloys probably would undergo intergranular corrosion in other highly oxidizing environments, and, as a result, the nature of the corrosive solution as well as the condition of the alloy must be considered. In austenitic stainless steels, niobium is also generally considered to be more effective than titanium in preventing intergranular attack under highly oxidizing conditions [*10*].

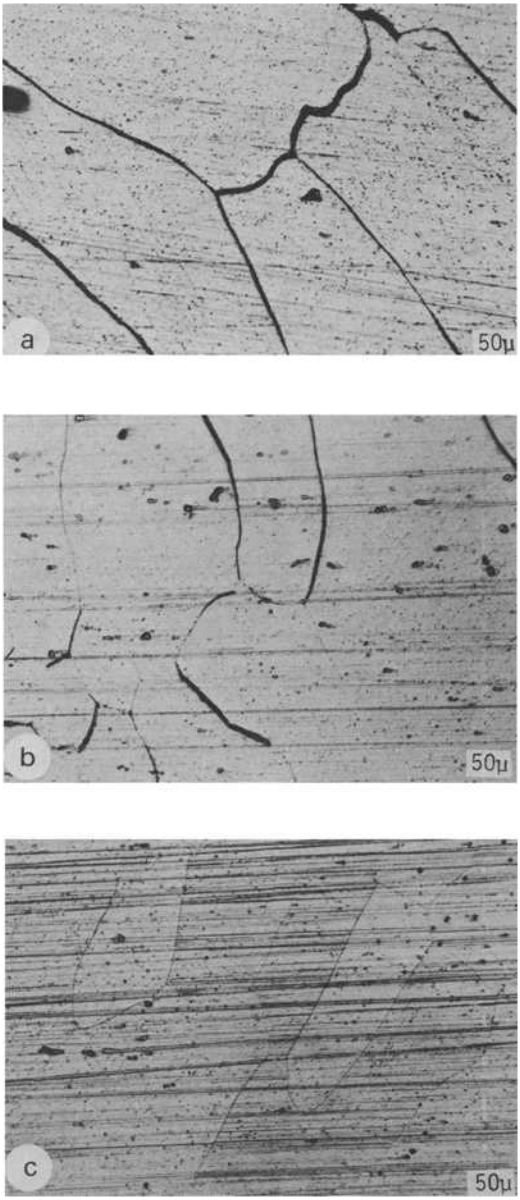
The oxalic acid etch test was successful in demonstrating the titanium or niobium stabilization of 26Cr-1Mo alloys and was in agreement with the other tests. The microstructures shown in Fig. 4 illustrate the transition of weld structure from an unstabilized to a stabilized condition with the unstabilized alloys having a groove structure and the stabilized alloys a flat structure. Of particular interest is the alloy containing 0.26 percent titanium which apparently represents a borderline stabilized condition and has a dual structure. This is a microstructure that has some groove structure, but no one grain is encircled by a groove structure. The presence of a dual stucture would indicate that the alloy has a discontinuous chromium-depleted zone that would not be detected easily in the other tests and yet could produce a lowered resistance to pitting corrosion which does not require a continuous chromium-depleted zone, as will be shown in a later section.

Exposure in 10 percent HNO_3-3 percent HF appeared to be successful in demonstrating stabilization of 26Cr-1Mo alloys, but the evaluation did require metallographic examination of the cross section of the corrosion specimen, since the amount of intergranular attack was insufficient to dislodge many of the surface grains (Fig. 5). All of the steels that were immune to intergranular corrosion in Cu-$CuSO_4$-16 percent H_2SO_4 had only

TABLE 3—*Resistance of autogenously welded 26Cr-1Mo alloys containing about 0.015% C and 0.015% N to intergranular corrosion in various tests.*

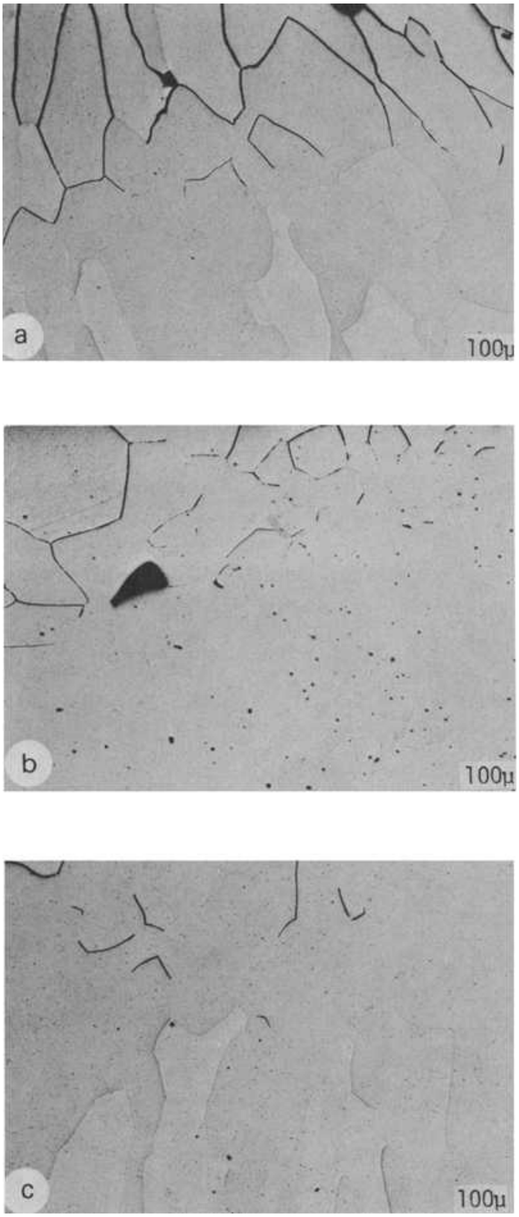
Alloy	Ti, %	$Cu-CuSO_4$-16% H_2SO_4	$Cu-CuSO_4$-50% H_2SO_4	$Fe_2(SO_4)_3$-50% H_2SO_4	10% HNO_3, 3% HF	Microstructure After 10% Oxalic Acid Etch Test
35a	0.17	fissuring	GD[a]	GD	IGA[b]	groove
35b	0.22	fissuring	GD	GD	IGA	groove
35c	0.26	no fissuring	no GD	GD	no IGA	dual
35d	0.30	no fissuring	no GD	GD	no IGA	flat
	Nb, %					
14a	0.09	fissuring	GD	GD	IGA	groove
14b	0.17	fissuring	GD	GD	IGA	groove
15a	0.33	no fissuring	no GD	no GD	no IGA	flat
15b	0.44	no fissuring	no GD	no GD	no IGA	flat

[a] Grain dropping.
[b] Intergranular attack.



(*a*) 0.22Ti Alloy 35b, groove structure.
(*b*) 0.26Ti Alloy 35c, dual structure.
(*c*) 0.30Ti Alloy 35d, flat structure.

FIG. 4—*Microstructure of weld cross section of 26Cr-1Mo-0.03(C + N) alloys containing titanium after exposure to 10 percent oxalic acid etch test.* ×*160.*



(*a*) 0.22Ti Alloy 35b.
(*b*) 0.09Nb Alloy 14a.
(*c*) 0.17Nb Alloy 14b.

FIG. 5—*Microstructure of unetched weld cross section of unstabilized 26Cr-1Mo-0.03 (C + N) alloys containing niobium or titanium after exposure to 10 percent HNO_3-3 percent HF test.* ×*80.*

uniform corrosion with no grain boundary penetration in the 10 percent HNO_3-3 percent HF test. Using a longer exposure time might allow an evaluation using loss of weight.

Accelerated Intergranular Corrosion Testing of Alloys Sensitized at 1205°C (2200°F)

Although it is usually preferable to test welds to determine if an alloy is stabilized, it may be useful to develop a sensitizing heat treatment to simulate the welding process. Thus, the effect of a 1205°C heat treatment in helium for 5 min followed by slow cooling on the corrosion resistance of ferritic stainless steels was determined. As shown in Tables 4 and 5, the use of the 1205°C (2200°F) heat treatment was successful in producing the same niobium and titanium requirements for 18Cr-2Mo and 26Cr-1Mo alloys as did autogenous welding. The alloys were evaluated in both Cu-$CuSO_4$-16 percent H_2SO_4 and Cu-$CuSO_4$-50 percent H_2SO_4.

TABLE 4—*Resistance of 18Cr-2Mo alloys containing about 0.03% (C + N) to intergranular corrosion in Cu-$CuSO_4$-16% H_2SO_4 test.*

Alloy	Ti, %	1205°C (2200°F) Heat Treatment	Autogenous Weld
17b	0.15	fissuring	fissuring
17c	0.19	fissuring	fissuring
20d	0.23	no fissuring	no fissuring
17d	0.26	no fissuring	no fissuring

TABLE 5—*Resistance of 26Cr-1Mo alloys containing about 0.03% (C + N) to intergranular corrosion.*

		Cu-$CuSO_4$-16% H_2SO_4 Test		Cu-$CuSO_4$-50% H_2SO_4 Test	
Alloy	Ti, %	1205°C (2200°F)	Autogenous Weld	1205°C (2200°F)	Autogenous Weld
35a	0.17	fissuring	fissuring	GD[a] (227 mdd)[b]	GD (67 mdd)
35b	0.22	fissuring	fissuring	GD (163 mdd)	GD (36 mdd)
35c	0.26	no fissuring	no fissuring	no GD (30 mdd)	no GD (14 mdd)
35d	0.30	no fissuring	no fissuring	no GD (29 mdd)	no GD (27 mdd)
	Nb, %				
14a	0.09	fissuring	fissuring	...	GD
14b	0.17	no fissuring	fissuring	...	GD
15a	0.33	no fissuring	no fissuring	...	no GD
15b	0.44	no fissuring	no fissuring	...	no GD

[a] Grain dropping.

[b] Corrosion rate in milligrams per square decimeter per day.

Based on the results, it would appear that this sensitizing heat treatment does simulate the heating effects of a weld and may be acceptable for evaluating the stabilization requirements for autogenously welded 18Cr-2Mo and 26Cr-1Mo alloys. The temperature of the sensitizing heat treatment, as well as the rate of cooling, can be very important. A previous study has shown that sensitizing at temperatures of 1150°C (2100°F) and lower does not produce a condition as severe as welding [*11*].

Resistance of Sensitized Alloys in Chloride Solution

A lowered resistance to corrosion in chloride-containing solutions can be related to susceptibility to intergranular corrosion [*12*]. Corrosion in chloride solutions may occur in unstabilized ferritic alloys by two means. First, pitting corrosion may be initiated at the intergranular chormium-depleted zone, and, as a result of accumulation of corrosion products, the pitting corrosion may extend into the sound weld metal. In less aggressive pitting environments, the pitting attack may be confined to the chromium-depleted zone and result in an intergranular attack similar to that experienced in the accelerated intergranular corrosion tests.

The exposure of autogenously welded 26Cr-1Mo alloys containing about 0.03 percent (C + N) in acidified 10 percent $FeCl_3$ illustrated the significant reduction in resistance to pitting corrosion that can occur with alloys that are susceptible to intergranular corrosion (Table 6). The results were in agreement with the Cu-$CuSO_4$-16 percent H_2SO_4 test with the exception of the alloy containing 0.26 percent titanium which, although being stabilized according to the Cu-$CuSO_4$-16 percent H_2SO_4 test, was subject to a small amount of pitting attack of the weld zone. This alloy also encountered a dual microstructure of the weld zone in the oxalic acid etch test, as shown

TABLE 6—*Resistance of autogenously welded 26Cr-1Mo alloys containing about 0.03% (C + N) to pitting corrosion.*

Alloy	Ti, %	10% $FeCl_3 \cdot 6H_2O$ + O.1*N* HCl at 25°C	Resistant to IGA[a] in Cu-$CuSO_4$-16% H_2SO_4 Test
35a	0.17	weld pitted (709 mdd)[b]	no
35b	0.22	weld pitted (543 mdd)	no
35c	0.26	weld pitted (9.2 mdd)	yes
35d	0.30	not pitted (1.0 mdd)	yes
	Nb, %		
14a	0.09	weld pitted (781 mdd)	no
14b	0.17	weld pitted (31 mdd)	no
15a	0.33	not pitted (0 mdd)	yes
15b	0.44	not pitted (0 mdd)	yes

[a] Intergranular attack.

[b] Corrosion rate in milligrams per square decimeter per day.

in Fig. 4. This suggests that the oxalic acid etch test which can detect the presence of a discontinuous chromium-depleted zone may be an important accelerated test to ensure that an alloy is resistant to pitting corrosion as well as intergranular attack. Attack in the unstabilized 26Cr-1Mo alloys exposed to acidified 10 percent $FeCl_3$ was not confined to the chromium-depleted grain boundaries but extended into the sound metal of the weld zone. Thus, pits initiated in the depleted zone may propagate into undepleted regions because of the autocatalytic nature of pitting. The amount of pitting attack of the weld decreased significantly as the niobium or titanium level was increased to that required for stabilization. The stabilized welded alloys were as resistant as in the annealed condition and apparently suffer no loss of corrosion from the welding process.

The effect in milder pitting environments is illustrated by the intergranular failure of stressed and unstabilized alloys when heat treated at 1205°C (2200°F) and exposed to boiling artificial seawater (Tables 7 and 8). Rapid

TABLE 7—*Resistance of U-bend specimens of 18Cr-2Mo alloys containing about 0.03% (C + N) to boiling seawater when heat treated at 1205°C (2200°F).*

Alloy	Ti, %	Failure Time, h	Resistant to IGA[a] in Cu-$CuSO_4$-16% H_2SO_4 Test
9a	0	2 to 18	no
17a	0.09	0 to 16	no
20a	0.11	0 to 16	no
17b	0.15	902[b]	no
17c	0.19	NF[c]	no
20d	0.23	NF	yes

[a] Intergranular attack.
[b] Small amount of intergranular attack.
[c] NF = tests discontinued with no cracks detectable after 902 h.

TABLE 8—*Resistance of U-Bend specimens of 26Cr-1Mo alloys containing about 0.03% (C + N) to boiling seawater when heat treated at 1205°C (2200°F).*

Alloy	Ti,%	Failure Time, h	Resistant to IGA[a] in Cu-$CuSO_4$-16% H_2SO_4 Test
35a	0.17	92 to 116	no
35b	0.22	452 to 500	no
35c	0.26	NF[b]	yes
	Nb, %		
14a	0.09	2 to 24	no
14b	0.17	NF	no
15a	0.33	NF	yes

[a] Intergranular attack.
[b] NF = tests discontinued with no cracks detectable after 902 h.

intergranular failure that was easily detected by visual examination of the specimen surface occurred on those 18Cr-2Mo and 26Cr-1Mo alloys that were unstabilized as shown by the Cu-$CuSO_4$-16 percent H_2SO_4 test and contained levels of niobium or titanium considerably lower that that required for stabilization. The alloys that were unstabilized but with levels of niobium and titanium approaching that needed for stabilization required much more time for the initial appearance of intergranular cracks. In these cases of long-term failure, the first visual evidence of corrosion was the occurrence of localized pitting at the eventual site of failure. In view of the apparently long period required for the localized pitting corrosion to initiate and progress into intergranular corrosion, the alloys which were shown to be not stabilized by the Cu-$CuSO_4$-16 percent H_2SO_4 test and were not subject to intergranular attack in boiling seawater cannot be assumed to be immune based on the test period used. Therefore, it must be concluded that an alloy which is not stabilized has a doubtful resistance to intergranular attack in boiling seawater.

To determine if the failure encountered in boiling seawater was a result of intergranular corrosion or stress corrosion cracking, an 18Cr-2Mo-0.022 (C + N) tensile specimen (Alloy 1) that had been sensitized at 1205°C (2200°F) was corroded in boiling seawater in an unstressed condition for 41 h. At the end of the exposure, the presence of intergranular corrosion on the surface of the gage section of the specimen was clearly evident. The corroded specimen was subjected to tensile testing using an elastic strain rate of 18 percent per hour and a plastic strain rate of 120 percent per hour to determine the effect of exposure in seawater on the mechanical properties. Elongation was reduced from 16 to 2 percent and ultimate stress reduced from 386 to 144 MPa (56 100 to 20 900 psi) as a result of the exposure. The substantial reduction in ductility and strength indicated that the failure process in seawater was the result of intergranular corrosion and not stress corrosion cracking.

A scanning electron photomicrograph of the fracture surface (Fig. 6) gave clear evidence of intergranular corrosion caused by the unstressed exposure in boiling seawater and cleavage failure due to the application of a tensile stress. The extent of penetration of intergranular corrosion in a corroded, but unstressed, condition is illustrated in Fig. 7. The penetration after a 41-h exposure in boiling seawater progressed more than halfway through the 4 mm (0.16 in.) thickness and provided further evidence that the failure was caused by intergranular corrosion.

Resistance of Sensitized Alloys in Formic Acid

The 18Cr-2Mo and 26Cr-1Mo alloys have particularly good resistance to organic acids. However, since their passivity does depend essentially on the chromium and molybdenum contents, the presence of a chromium-

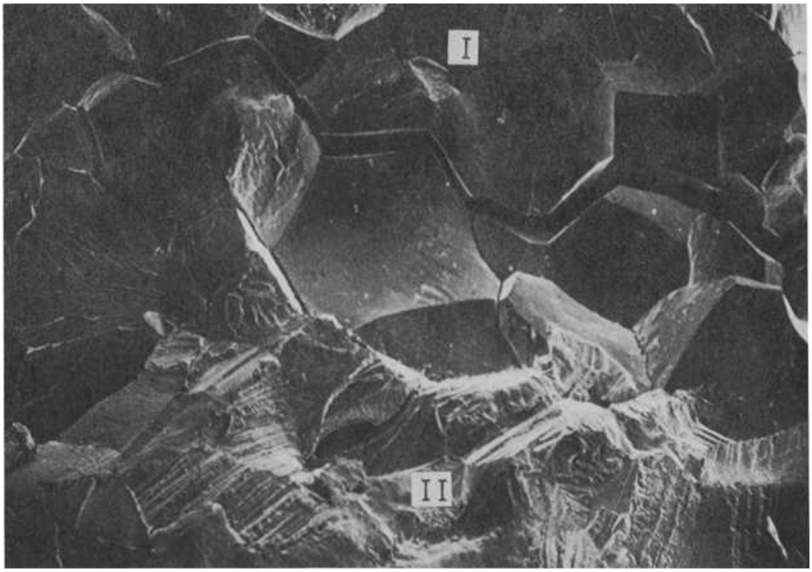


FIG. 6—*SEM photograph of fracture surface of an 18Cr-2Mo-0.018C-0.004N alloy (1) sensitized at 1205°C (2200°F), exposed with no applied stress in boiling seawater for 41 h and fractured by a tensile load. Note the transition from intergranular corrosion (I) to cleavage failure (II).* ×*40.*

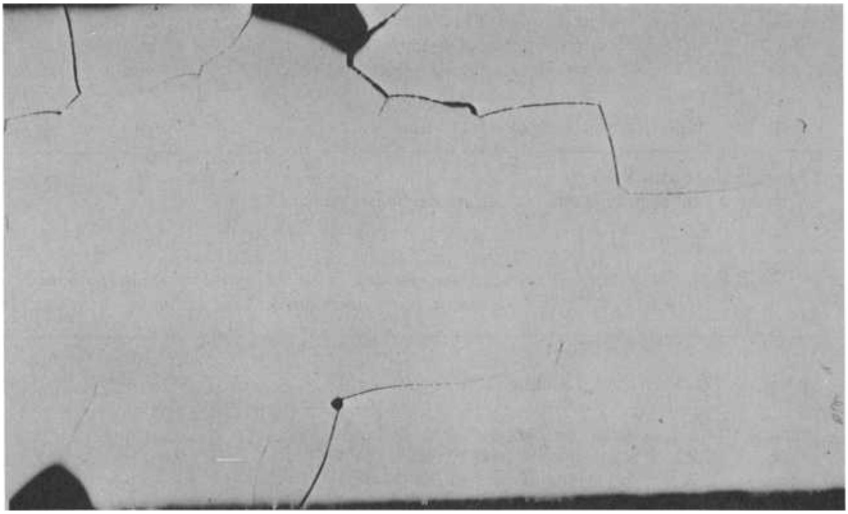


FIG. 7—*Unetched cross section of 18Cr-2Mo-0.018C-0.004N alloy (1) sensitized at 1205°C (2200°F) and exposed to boiling seawater for 41 h.* ×*23.*

depleted zone will result in a significantly reduced resistance. The practical aspect of the presence of the chromium-depleted zone as the result of an unstabilized condition is illustrated by exposure in boiling formic acid (Tables 9, 10). The autogenously welded 18Cr-2Mo and 26Cr-1Mo alloys that were not stabilized as shown by the Cu-$CuSO_4$-16 percent H_2SO_4 test were subject to intergranular corrosion in boiling 20 and 80 percent formic acid. The stabilized alloys were either immune to attack or had a small amount of uniform corrosion. The unstabilized 18Cr-2Mo alloy containing 0.11 percent titanium and 26Cr-1Mo alloy containing 0.17 percent titanium were subject to grain dropping in both the heat-affected zone and weld as shown in Figs. 8 and 9. The 18Cr-2Mo alloy containing no titanium was subject to such severe intergranular attack that the weld was entirely removed.

Discussion

The results of exposure in the Cu-$CuSO_4$-16 percent H_2SO_4 test established that autogenously welded 18Cr-2Mo and 26Cr-1Mo alloys containing up to 0.10 percent (C + N) can be stabilized with either niobium or ti-

TABLE 9—*Resistance of autogenously welded 18Cr-2Mo alloys containing about 0.03% (C + N) to corrosion in an organic acid for 24 h.*

Alloy	Ti, %	Boiling 20% Formic Acid	Resistant to IGA[a] in Cu-$CuSO_4$-16% H_2SO_4 Test
8a	0	weld dissolved (30 300 mdd)[b]	no
19	0.11	grain dropping of weld (693 mdd)	no
25a	0.27	no attack of weld (58 mdd)	yes
	Nb, %		
9b	0.30	no attack of weld (0 mdd)	yes

[a] Intergranular attack.

[b] Corrosion rate in milligrams per square decimeter per day.

TABLE 10—*Resistance of autogenously welded 26Cr-1Mo alloys containing about 0.03% (C + N) to corrosion in an organic acid for 120 h.*

Alloy	Ti, %	Boiling 80% Formic Acid	Resistant to IGA[a] in Cu-$CuSO_4$-16% H_2SO_4 Test
35a	0.17	grain dropping of weld (163 mdd)[b]	no
35b	0.22	etching of weld (127 mdd)	no
35c	0.26	no attack of weld (0 mdd)	yes
35d	0.30	no attack of weld (0 mdd)	yes

[a] Intergranular attack.

[b] Corrosion rate in milligrams per square decimeter per day.

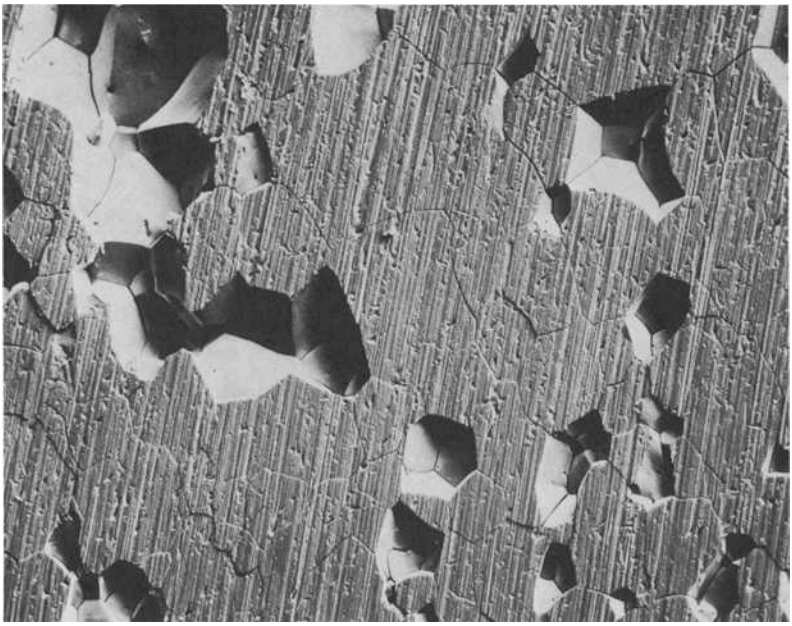


FIG. 8—*Grain dropping from the weld zone surface of an 18Cr-2Mo-0.11Ti alloy (19) containing about 0.03 percent (C + N) after a 24-h exposure to boiling 20 percent formic acid. ×110.*

tanium to prevent intergranular corrosion. The amount of stabilizer required for the 26Cr-1Mo alloys was consistent with that which would be predicted from the results of the 18Cr-2Mo alloy.

Although weld ductility was not evaluated in detail, all materials that passed the Cu-$CuSO_4$-16 percent H_2SO_4 test did sustain a 1 *T* transverse bend, indicating reasonably good weld ductility.

The stabilization requirements were supported by accelerated intergranular corrosion tests in Cu-$CuSO_4$-50 percent H_2SO_4, $Fe_2(SO_4)_3$-50 percent H_2SO_4, 10 percent HNO_3-3 percent HF, and the 10 percent oxalic acid etch test. Pitting tests in acidified 10 percent $FeCl_3$ were also in agreement. Unstabilized alloys were subjected to intergranular corrosion in other solutions that represent service applications such as boiling seawater and boiling formic acid. Although only a few solutions representing practical service were studied, it can be generalized that alloys susceptible to intergranular corrosion in laboratory accelerated tests are not suitable for application involving exposure to corrosive environments.

The good agreement between the ASTM A 262 accelerated intergranular corrosion tests, the acidified 10 percent $FeCl_3$ test, and exposure in boiling seawater and boiling formic acid is considered particularly important be-

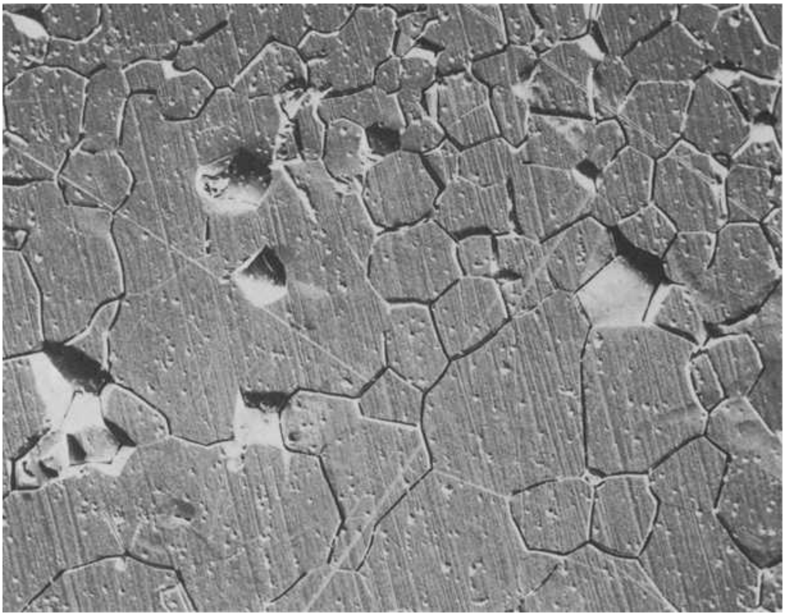


FIG. 9—*Grain dropping from the weld zone surface of a 26Cr-1Mo-0.17Ti alloy (35a) containing about 0.03 percent (C + N) after 120-h exposure to boiling 80 percent formic acid.* ×*110.*

cause of the difficulty that has been experienced in establishing an acceptance test for the evaluation of stabilization of welded ferritic stainless steel. Based upon the ease of testing and evaluation, either the Cu-$CuSO_4$-16 percent H_2SO_4 test or the Cu-$CuSO_4$-50 percent H_2SO_4 test are acceptable choices. However, the oxalic acid etch test may provide some unique advantages such as rapid evaluation and possible portability for the nondestructive evaluation of welded surfaces. In addition, the ability of the oxalic acid etch test to detect a discontinuous chromium-depleted zone may be important with regard to resistance to pitting corrosion. It would appear that the use of the $Fe_2(SO_4)_3$-50 percent H_2SO_4 test should be limited to those cases where the use of the alloy would involve highly oxidizing conditions.

Since it is clear that either niobium or titanium will produce stabilization, the choice of which stabilizer to use depends on the application for which the alloy is intended. Both the type and amount of stabilizer are important factors in obtaining optimum toughness and weld ductility as well as resistance to intergranular and pitting corrosion. In general, weld ductility is greater in titanium-stabilized alloys, and the impact toughness is greater in niobium-stabilized alloys; titanium or niobium greatly in excess of that minimum amount required for stabilization, Nb or Ti = 0.20 percent + 4 (C + N), can reduce these properties [*13*].

It is possible that a mixture of titanium and niobium can be used for stabilization to achieve the optimum balance needed to obtain both improved weld ductility and impact toughness. With regard to intergranular corrosion resistance, niobium stabilization is effective even in highly oxidizing environments such as concentrated nitric acid; titanium stabilization is only effective in less oxidizing environments [*14*]. Titanium stabilization produces a slightly better pitting resistance than niobium stabilization if the environment is not highly oxidizing [*15*].

Conclusions

It has been demonstrated that the failure to provide stabilization in autogenously welded 18Cr-2Mo and 26Cr-1Mo alloys will result in welds having a greatly lowered resistance to intergranular corrosion in a wide variety of corrosive environments and to pitting corrosion.

Stabilization can be provided in these alloys by the addition of sufficient amounts of niobium or titanium to provide a weld that has a corrosion resistance similar to that of the base metal. The recommended minimum addition to produce stabilization for 18Cr-2Mo alloys containing 0.02 to 0.05 percent (C + N) is Nb or Ti = 0.20 percent + 4 (C + N).

The Cu-$CuSO_4$-16 percent H_2SO_4 or the Cu-$CuSO_4$-50 percent H_2SO_4 tests are preferred for the evaluation of welded 18Cr-2Mo and 26-Cr-1Mo alloys. The $Fe_2(SO_4)_3$-50 percent H_2SO_4 test, which produced grain dropping from the welds of titanium-stabilized alloys, is not suitable for general use with the 18Cr-2Mo or 26Cr-1Mo alloys.

Of particular interest is the 10 percent oxalic acid etch test which may provide a rapid means of determining whether an alloy is stabilized. The test may also be suitable for nondestructive, on-site testing of welds that may have been contaminated with nitrogen or carbon during the welding process.

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Intergranular Corrosion Testing and Sensitization of Two High-Chromium Ferritic Stainless Steels

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REFERENCE: Nichol, T. J. and Davis, J. A., "**Intergranular Corrosion Testing and Sensitization of Two High-Chromium Ferritic Stainless Steels,**" *Intergranular Corrosion of Stainless Alloys, ASTM STP 656,* R. F. Steigerwald, Ed., American Society for Testing and Materials, 1978, pp. 179–196.

ABSTRACT: The effect of several parameters (alloy chemistry, thermal history, and solution chemistry) on the resistance of two new ferritic stainless steels to intergranular corrosion was investigated. The susceptibility of Types 26-1S and 29-4 to intergranular corrosion depended on the alloy chemistry and the particular test used to evaluate susceptibility. For both alloys, the severity of the standard tests increased in the following order: copper sulfate ($CuSO_4$)-16 percent sulfuric acid (H_2SO_4), nitric acid (HNO_3)-hydrogen fluoride (HF), $CuSO_4$-50 percent H_2SO_4 and ferric sulfate ($Fe_2(SO_4)_3$)-50 percent H_2SO_4. Sensitization was produced in these alloys by either welding or high-temperature annealing followed by air cooling. The most reliable evaluation method was bending of the material combined with optical examination.

KEY WORDS: stainless steels, intergranular corrosion, ferritic stainless steels, sensitizing, evaluation, tests

The susceptibility of conventional ferritic stainless steels to intergranular corrosion after welding operations has been one of the major problems preventing extensive utilization of these steels. The sensitized regions of ferritic stainless steel weldments are normally the weld metal itself and a narrow region adjacent to the weld metal. The mechanism responsible for intergranular corrosion is generally accepted as being the same as that in austenitic stainless steels. The formation of chromium compounds, usually carbides or nitrides or both, at the grain boundaries results in the creation of chromium-depleted regions adjacent to the grain boundary particles [*1*].[2] Intergranular corrosion occurs because of the relative difference

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

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in corrosion resistance between the chromium-depleted regions and the matrix.

Lula, Lena, and Kiefer [*2*] suggested that intergranular corrosion could be prevented in ferritic stainless steels by lowering the carbon content or by stabilizing the carbon with titanium. Two newer ferritic stainless steels which represent these alternatives are Type 26-1S [*3*], a 26Cr-1Mo steel stabilized with titanium, and Type 29-4 [*4*], a 29Cr-4Mo steel melted to low levels of both carbon and nitrogen. Bond and Dundas [*5*] have determined the amount of titanium required in ferritic stainless steels to prevent intergranular corrosion in a boiling copper sulfate-sulfuric acid ($Cu\ SO_4$-$H_2\ SO_4$) solution. For 26Cr-1Mo alloys having combined carbon and nitrogen levels up to 0.04 percent, they claim the minimum titanium necessary to prevent intergranular corrosion is equal to 0.15 percent plus 3.7 times the carbon plus nitrogen content. Pollock, Sweet, and Collins [*6*] also investigated the intergranular corrosion resistance of Type 26-1S and concluded that a minimum titanium ratio of ten times the carbon plus nitrogen contents is preferred to provide resistance. ASTM specifications for Type 26-1S (ASTM Grade XM33) list a minimum titanium of seven times the carbon plus nitrogen content. Lula et al [*2*] demonstrated that ferritic stainless steels containing titanium were resistant to intergranular corrosion in the boiling $Cu\ SO_4$-$H_2\ SO_4$ solution but not to boiling 65 percent nitric acid (HNO_3). Baumel [*7*] subsequently showed that titanium carbides were attacked directly by boiling 65 percent HNO_3. Streicher [*4*] used a boiling ferric sulfate ($Fe_2(SO_4)_3$)-$H_2\ SO_4$ solution to determine the carbon and nitrogen contents necessary to prevent intergranular corrosion of welded 28Cr-4Mo alloys. The levels determined were 100 ppm for carbon and 200 ppm for nitrogen, with the additional requirement that the total carbon plus nitrogen must be less than 250 ppm.

Several studies [*1, 2, 8–15*] have utilized various heat treatments (other than welding) to produce sensitization in ferritic stainless steels. The critical parameters are temperature, time at temperature, and cooling rate from elevated temperatures. Three temperatures are important for sensitization: an elevated temperature (referred to as the sensitization temperature) which corresponds to the temperature where significant amounts of carbon and nitrogen are soluble in the ferrite matrix, an intermediate temperature where titanium and columbium carbides and nitrides form, and a lower temperature which corresponds to the temperature at which chromium carbides and nitrides form. Time at temperature controls both the dissolution process (at or above the sensitization temperature) and the degree of chromium depletion (at the precipitation temperature). Cooling rates from the sensitization temperature or higher control the balance between chromium depletion resulting from precipitation and chromium leveling resulting from chromium diffusion [*12*].

The difference in corrosion rate between chromium-depleted regions and the ferritic matrix has been attributed to simply the dependence of the passive corrosion rate on the chromium content of the ferrite.

Streicher [*14*] and Steigerwald [*15*] demonstrated the very large effect of chromium content on the general corrosion rate (in the passive state) in a boiling $Fe_2(SO_4)_3$-H_2SO_4 acid solution. Streicher's [*14*] work demonstrated that chromium-depleted regions are probably less than 25 percent chromium in high-chromium ferritic steels and greater than 12 percent chromium in 16 percent chromium steels. Streicher also emphasized that the effectiveness of any solution in delineating susceptibility to intergranular corrosion depends on sensitivity of that solution to chromium content. Bond [*1*] and Bond and Lizlovs [*9*] demonstrated that sensitized and nonsensitized ferritic stainless steels exhibit different anodic polarization characteristics in 1 N H_2SO_4. They found that the peak corresponding to active dissolution is unaffected by sensitization; however, sensitized steels exhibited a secondary peak in the passive range as well as higher current densities than nonsensitized steels. Anodic polarization only showed effects of sensitization resulting from carbon increases and not nitrogen.

These studies have shown that the susceptibility of ferritic stainless steels to intergranular corrosion depends on (*a*) the corrosive media in which the steels are exposed, (*b*) the chemistry (particularly carbon and nitrogen) of the steel, and (*c*) the thermal history of the steel.

The purpose of this study was to investigate the parameters (chemistry, thermal history, and solution chemistry) which determine the susceptibility of two new ferritic stainless steels to intergranular corrosion. The initial work utilized welded materials having variable compositions previously determined [*4*, *5*] in one standard test to represent both resistant and susceptible material. The behavior of welded specimens in four standard laboratory intergranular corrosion tests was determined. In addition, the effects of sensitization temperature and cooling rate were investigated for the different compositions of material. Finally, anodic polarization studies in $CuSO_4$-50 percent H_2SO_4 were conducted.

Experimental Procedure

Materials and Preparation

Strip material 0.17 cm (65 mil) thick from several heats of Types 26-1S and 29-4 was obtained in the annealed condition 387 cm per minute per centimetre of thickness (60 in. per minute per inch of thichness) at 954°C (1750°F) for Type 26-1S and 1066°C (1950°F) for Type 29-4). The Type 26-1S material represented a range of compositions from Ti/C+N = 3.5 to Ti/C+N = 18.5, while the Type 29-4 encompassed compositions from 34 to 380 ppm of carbon and 27 to 265 ppm of nitrogen. The specific carbon, nitrogen, and titanium levels are tabulated in the Results section of this paper. Welded specimens were prepared using conventional tungsten inert gas procedures. Helium was used as the shielding and backup gas. Heat treatments were conducted in a furnace containing an argon atmosphere. All specimens were machined (both edges and surface) to a standard 5.1 by 2.5 by 0.15 cm (2 by 1 by 0.060 in.) size having a 50 rms surface finish. All specimens were degreased in hot alkaline cleaner rinsed in distilled water, dipped in methanol, dried, and weighed prior to testing.

Corrosion Tests

Cupric Sulfate Test—This test was conducted in accordance with ASTM Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels (A 262, Practice E). Specimens were exposed to a boiling aqueous solution of 6 percent by weight $CuSO_4$ plus 16 percent by weight H_2SO_4 for a 24-h period. The specimens were in galvanic contact with copper shot.

Nitric Acid-Hydrofluoric Acid (HF) Test—This test, except for exposure time, was conducted in accordance with ASTM A 262, Practice D. Duplicate specimens were tested in a 10 percent HNO_3-3 percent HF solution at 70°C (158°F) for two 4-h periods (a fresh solution was used for each period).

Modified Cupric Sulfate Test—This test, except for solution chemistry [*16*], was conducted in accordance with ASTM A 262, Practice B. Specimens were exposed for one period of 120-h duration in a boiling solution consisting of 71.4 g of reagent grade $CuSo_4 \cdot 5H_2O$ and 600 ml of 50 percent H_2SO_4. A clean, solid piece of copper was immersed in the solution (not in contact with the specimens) throughout the test period. The first use of this test for Type 26-1S was described by Pollock et al [*6*].

Ferric Sulfate Test—This test was conducted in accordance with ASTM A 262, Practice B. Specimens were exposed for one period of 120-h duration in a boiling solution consisting of reagent grade $Fe_2(SO_4)_3$ and 50 percent H_2SO_4.

Polarization Tests—Anodic polarization measurements were conducted in a glass cell modified for sheet specimens. Specimens were clamped against a circular Teflon[3] gasket, exposing 1 cm^2 of surface area to the corrosive media. A platinized platinum electrode was used for a counter electrode, and a saturated calomel electrode was used as a reference electrode with potentials recorded through a salt bridge. Anodic polarization curves were run potentiodynamically at a scan rate of 32 V/h. The rapid scan rate was used to avoid extensive dissolution in the active region of the anodic polarization curve. Anodic polarization curves were generated in boiling 2 *N* H_2SO_4 and in the four intergranular test solutions. Activa-

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[3] Trade name of the du Pont de Nemours Company.

tion areas were determined by measuring the area under the primary active anodic peak or the secondary active anodic peak.

Evaluation Procedures

All specimens were weighed after testing and a corrosion rate determined. Specimens were also examined at ×30 magnification for evidence of grain dropping. In addition, most specimens were bent through 180 deg around a radius equal to the specimen thickness and examined for cracks or fissures.

Welded specimens were rated as passed (that is, resistant to intergranular corrosion) if no grain dropping was observed at ×30 and no cracks or fissures were observed after bending. A failure thus constituted either grain dropping or fissures on bending. Corrosion rates were not used for evaluation of welded specimens.

Heat-treated specimens were evaluated in a fashion similar to welded specimens; however, correlations between corrosion rate and evidence of intergranular corrosion were made.

Results

Table 1 lists the results for welded Type 26-1S material in the four different evaluation tests. All materials subjected to the $Fe_2(SO_4)_3$-50 percent H_2SO_4 test failed. The results for the three other tests delineate three areas of behavior. Materials having a Ti/C+N ratio lower than 6 failed all three tests. Materials having a Ti/C+N ratio between 6 and 9 demonstrated different responses, depending on the particular test that, is, the same material may pass one test and fail the other two. Materials having a Ti/C+N ratio greater than 9 passed the three tests. Figure 1 shows the appearance of the bent materials having Ti/C+N ratios of 5.4, 6.2, 7.4, and 9.1 after testing in the three different tests. The variable response of the materials having Ti/C+N ratios of 6.2 and 7.4 is evident.

Table 2 lists the results for welded Type 29-4 material in the four evaluation tests. Although the results from test to test are more consistent than the welded Type 26-1S results (Table 1), there is still disagreement between the tests for two heats. In this case, the two heats passed the $CuSO_4$-16 percent H_2SO_4 test and failed the three other tests. The Type 29-4 materials can be also delineated into the three areas, that is, materials that pass all the tests, materials that fail all the tests, and materials whose resistance is dependent on the test.

Figure 2 shows the bent specimens from two heats of Type 29-4 in the four evaluation tests. All the tests except the $CuSO_4$-16 percent H_2SO_4 test resulted in very definitive grain dropping in the heat-affected zone of the material having 100 ppm of carbon and 150 ppm of nitrogen. The

TABLE 1—*Results for welded Type 26-1S.*

Composition, percent by weight							
C	N	Ti	Ti/C+N	Test 1 $CuSO_4$ 16% H_2SO_4	Test 2 HNO_3 HF	Test 3 $CuSO_4$ 50% H_2SO_4	Test 4 $Fe_2(SO_4)_3$ 50% H_2SO_4
0.017	0.031	0.17	3.5	F	F	F	F
0.017	0.031	0.26	5.4	F	F	F	F
0.028	0.037	0.40	6.2	P	F	F	NT
0.024	0.030	0.40	7.4	P	P	F	NT
0.030	0.019	0.38	7.8	P	P	F	F
0.041	0.034	0.62	8.3	P	P	F	NT
0.019	0.030	0.42	8.6	P	P	F	F
0.025	0.019	0.40	9.1	P	P	P	NT
0.024	0.028	0.52	10.0	P	P	P	NT
0.073	0.017	1.06	11.8	P	P	P	NT
0.020	0.024	0.57	13.0	P	P	P	F
0.040	0.018	0.77	13.3	P	P	P	NT
0.012	0.017	0.44	15.2	P	P	P	NT
0.054	0.010	1.06	16.6	P	P	P	F
0.020	0.020	0.74	18.5	P	P	P	F

NOTE— P—no grain dropping or fissures on bending.
F—grain dropping or fissures on bending.
NT—not tested.

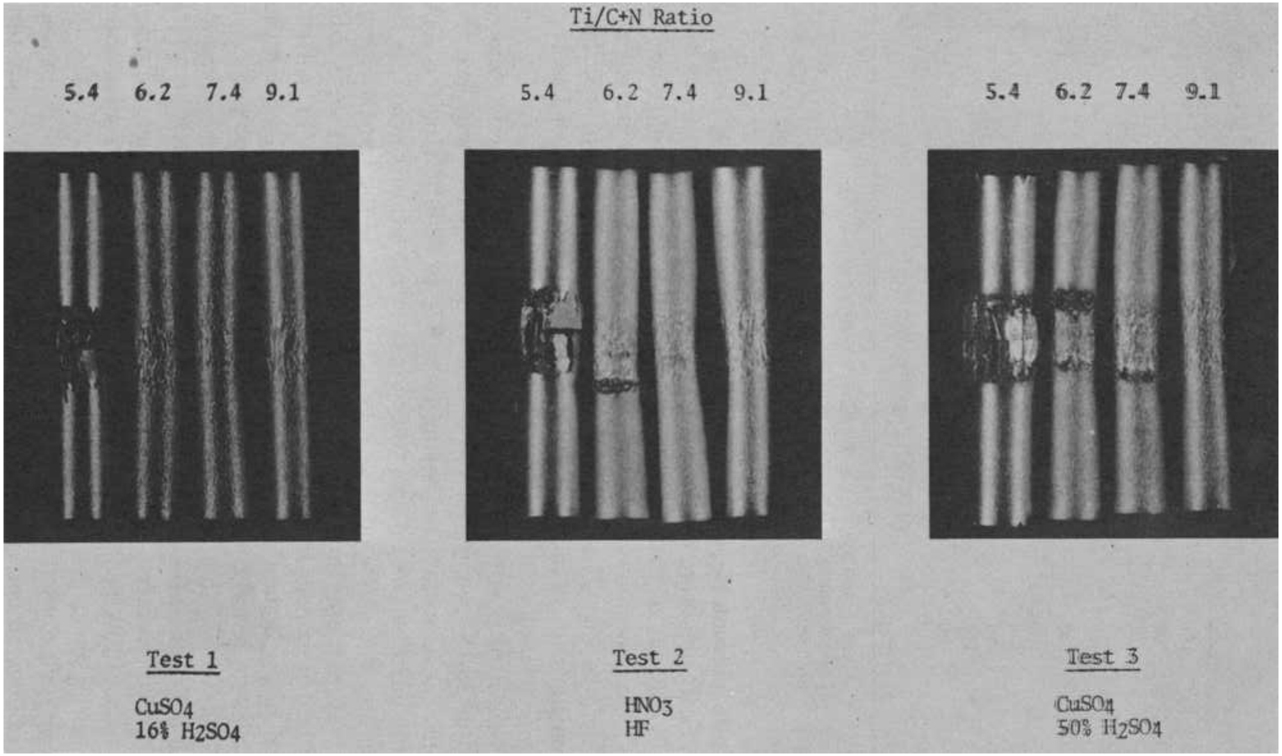

FIG. 1—*Effect of Ti/C + N ratio and evaluation test on the susceptibility of welded Type 26-1S specimens to intergranular corrosion.*

TABLE 2—*Results for welded Type 29-4.*

Composition, ppm			Test 1 $CuSO_4$	Test 2 HNO_3	Test 3 $CuSO_4$	Test 4 $Fe_2(SO_4)_3$
C	N	C+N	16% H_2SO_4	HF	50% H_2SO_4	50% H_2SO_4
380	150	530	F	F	F	F
180	160	340	F	F	F	F
110	38	148	NT	NT	F	F
100	150	250	P	F	F	F
45	265	310	P	F	F	F
42	250	292	P	P	P	P
46	190	236	P	P	P	P
44	118	162	P	P	P	P
40	150	190	P	P	P	P
16	140	156	P	P	P	P
34	27	61	P	P	P	P

NOTE—P = no grain dropping or fissures on bending.
F = grain dropping or fissures on bending.
NT = not tested.

$CuSO_4$-16 percent H_2SO_4 test did not result in grain dropping, and no cracks or fissures were evident after bending. The appearance of the weld metal is a result of the bending. This is similar to an orange-peel effect that is commonly observed after deformation of material having a large grain size. In Fig. 2, the material having 42 ppm carbon and 250 ppm nitrogen shows this orange-peel effect; however, no cracks or fissures were present.

The effect of heat-treatment temperature and cooling rate were determined for 26-1S having a Ti/C + N ratio of 7.8. Material was heat treated for 5 min at temperatures ranging from 871 to 1260°C (1600 to 2300°F) and then quenched into water, cooled in ambient air, or cooled in a bed of vermiculite. The corrosion rates were determined in the $CuSO_4$-50 percent H_2SO_4 test and are shown in Fig. 3. Higher corrosion rates were observed as the heat-treatment temperature exceeded 1038°C (1900°F). Air cooling resulted in the highest corrosion rates. Both water quenching and cooling in vermiculite reduced the corrosion rates for material heat treated above 1038°C (1900°F). In addition, water quenching raised the apparent sensitization temperature. Figure 4 illustrates the effect of Ti/C + N ratio on the corrosion rate in $CuSO_4$-50 percent H_2SO_4 after elevated temperature exposure followed by air cooling. The apparent sensitization temperature is increased as the Ti/C + N ratio is increased.

Anodic polarization curves are shown in Fig. 5 for 26-1S exposed to boiling $CuSo_4$-50 percent H_2SO_4. The curves shown in Fig. 5 are for material having Ti/C + N ratios of 7.8 and 11.8, and heat treated at 1149°C

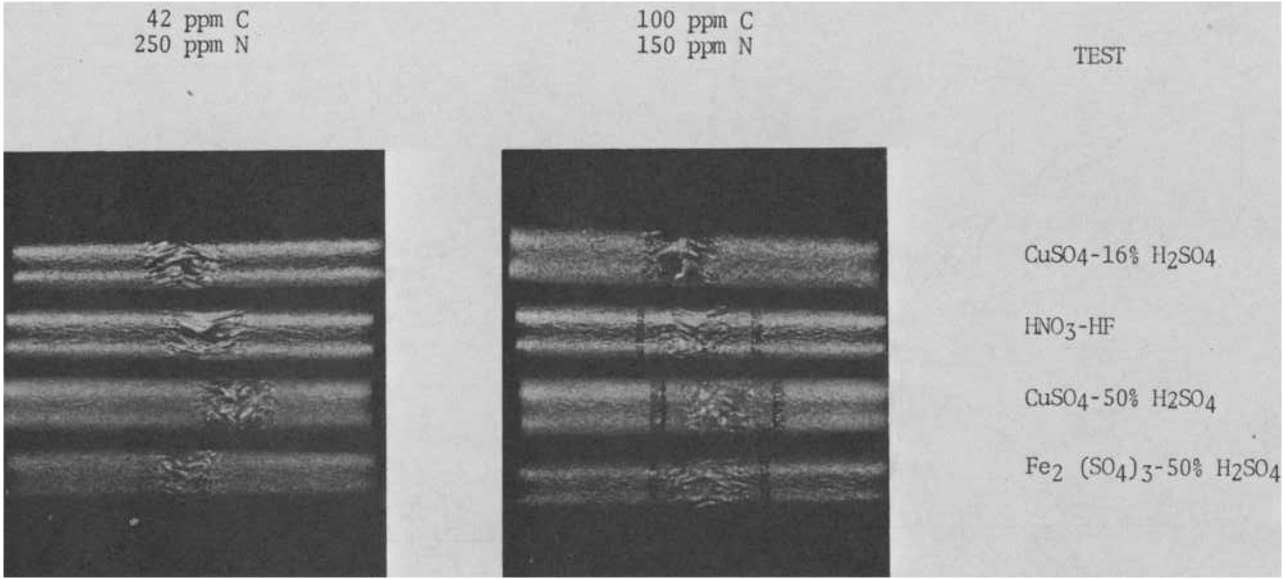

FIG. 2—*Effect of carbon, nitrogen, and evaluation test on the susceptibility of welded Type 29-4 material to intergranular corrosion (1.0 mil/year = 2.5 × 10^{-2} mm/A).*

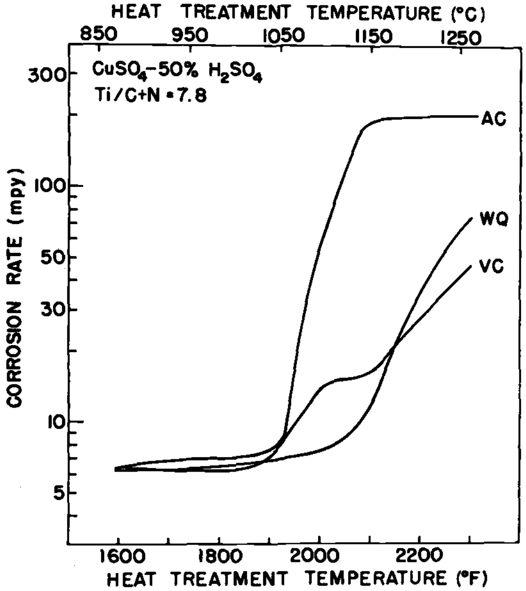

FIG. 3—*Effect of cooling rate and heat-treatment temperature on the corrosion rate of Type 26-1S. AC = air cool, WQ = water quench, VC = vermiculite cool (1.0 mil/year = 2.5 × 10^{-2} mm/A).*

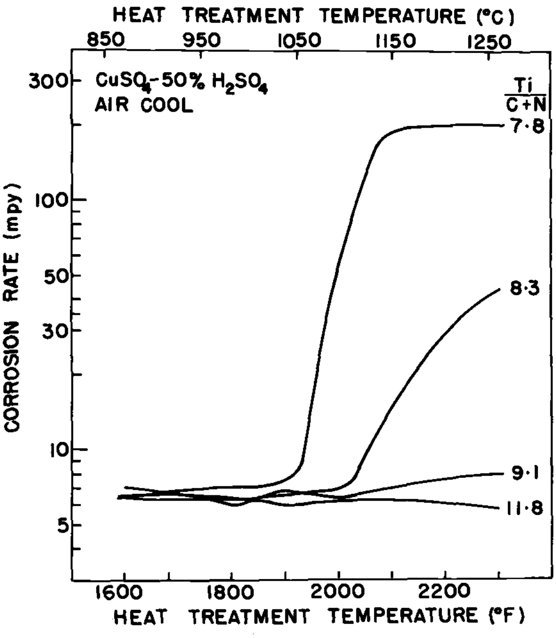

FIG. 4—*Effect of temperature and Ti/C+N ratio on the corrosion rate of Type 26-1S.*

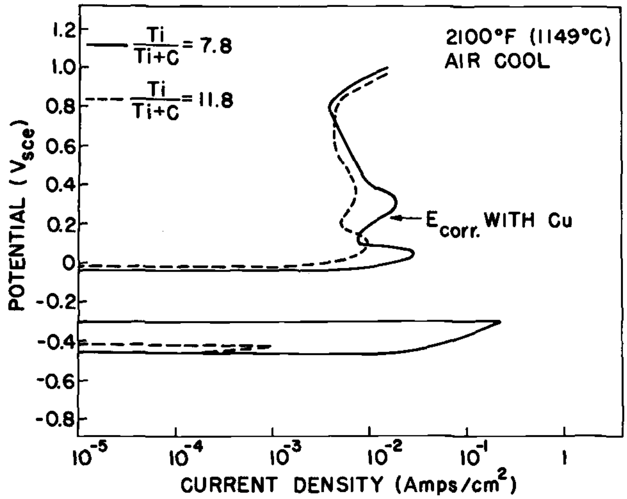

FIG. 5—*Effect of Ti/C+N on the anodic polarization of Type 26-1S in* $CuSO_4$*-50 percent* H_2SO_4.

(2100°F), followed by cooling in air. The critical current density, primary activation area, and secondary activation area were determined for the four Ti/C+N ratios shown in Fig. 4 for the 1149°C (2100°F) heat treatment, and the primary activation area as a function of Ti/C+N is shown in Fig. 6. A semilog relationship was observed between primary activation area and Ti/C+N.

The results in Table 3 illustrate the effect of elevated temperature (5 min at temperature) and cooling rate (air cool or water quench) on the corrosion rate of several Type 29-4 heats in the $Fe_2(SO_4)_3$-50 percent H_2SO_4 test. Water quenching again raises the apparent sensitization temperature (for the 180-ppm carbon material) and decreases the corrosion rate at all temperatures. The susceptibility of the 29-4 heats to high corrosion rates is more sensitive to the carbon content than the nitrogen content. This effect is shown in Fig. 7 for material heat treated at 1121°C (2050°F), air cooled, and tested in either the $Fe_2(SO_4)_3$-50 percent H_2SO_4 solution or the $CuSO_4$-50 percent H_2SO_4 solution. The materials having variable carbons contained approximately 150 ppm of nitrogen, while the materials having variable nitrogen contained approximately 40-ppm carbon. There is good correlation between the corrosion rates determined in $CuSO_4$-50 percent H_2SO_4 test and the $Fe_2(SO_4)_3$-50 percent H_2SO_4 test.

The effect of heat treating in the low-temperature sensitizing range was determined at one temperature 593°C (1100°F) for three heats of Type 29-4. Material was initially heat treated at 1121°C (2050°F) and then water quenched. The effect of time at 593°C (1100°F) on the corrosion rate in the $Fe_2(SO_4)_3$-50 percent H_2SO_4 test is shown in Fig. 8. The high-carbon material (110 ppm) demonstrated an increased corrosion rate after 30 min, followed by a decrease in corrosion rate for longer times. The high corrosion rate at 30 min was much less than the corrosion rate observed when this material was air cooled from 1121°C (2050°F) (Table 3). The high-nitrogen material (250 ppm) demonstrated a relatively constant corrosion rate up to 100 min and then increased slightly after 300 min. The corrosion rate of the low-carbon (34 ppm) and nitrogen (27 ppm) material was not affected by time at 593°C (1100°F).

The effect of the different tests on the corrosion rates of several 29-4 heats is shown in Table 4. All materials were heat treated at 1121°C (2050°F) and air cooled. For material that is resistant to intergranular corrosion, the corrosion rates for the HNO_3-HF test, the $CuSO_4$-50 percent H_2SO_4 test, and the $Fe_2(SO_4)_3$-50 percent H_2SO_4 test are similar, while the $CuSO_4$-16 percent H_2SO_4 test results in corrosion rates that are an order of magnitude lower. For material that is susceptible to intergranular corrosion, the corrosion rates increase in the order: $CuSO_4$-16 percent H_2SO_4 test, HNO_3-HF test, $Fe_2(SO_4)_3$-50 percent H_2SO_4 test, and $CuSO_4$-50 percent H_2SO_4 test. The corrosion rate in the $CuSO_4$-50 percent H_2SO_4 test is one to three orders of magnitude higher than the corrosion rate in the $CuSO_4$-16 percent H_2SO_4 test.

Discussion

The requirement for reliable laboratory intergranular corrosion tests and evaluation criteria designed specifically for ferritic stainless steels has developed with the introduciton of several new ferritic stainless steels. Reliable laboratory tests are required in the development stage to delineate the required compositional limits for the alloys and in the commercial product stage to establish product acceptance criteria. The data in Tables 1 and 2, for Types 26-1S and 29-4, clearly show that the present laboratory intergranular corrosion tests do not yield comparable results when the same materials are tested in the as-welded condition. If the number of materials that failed a given test is used as a measure of test severity, then the tests increase in severity from Test 1 to 2 to 3 to 4.

Both Types 26-1S and 29-4 have compositonal ranges which represent materials that either pass all tests or fail all tests. The intermediate composition ranges (characterized by varied results from test to test) are the composition of concern. In order to determine the suitability of materials within these compositional ranges for use in the as-welded condition, the laboratory tests will have to be supplemented by and correlated with actual service enviroments. The results indicate that, for Type 26-1S, there is a minimum ratio of $Ti/C+N$ required to provide intergranular corrosion resistance, and the absolute minimum level depends on the evaluation test

TABLE 3—*Effect of heat treatment on the corrosion rate (mil/year)*[c] *of Type 29-4 in* $Fe_2(SO_4)_3$*-50%* H_2SO_4.

Composition, ppm			Water Quench			Air Cool		
C	N	C+N	1010°C (1850°F)	1121°C 2050°F)	1232°C (2250°F)	1010°C 1850°F)	1121°C 2050°F)	1232°C 2250°F)
40	150	190	4.0	4.7	5.8	4.5	5.2	6.0
100	150	250	3.8	5.7	3.9	8.2	47.3[b]	64.4[b]
180	160	340	4.0	4.4[b]	21.2[b]	5.3	127.1[b]	D[a]
110	38	148	3.9	7.6[b]	5.5[b]	4.6	51.0[b]	D[a]
34	27	61	4.0	4.5	4.4	3.9	5.0	6.0
40	150	190	4.0	4.7	5.8	4.5	5.2	6.0
42	250	292	3.8	4.4	5.9	4.5	5.1	7.5[b]
45	265	310	3.0	7.7[b]	3.7	5.0	7.6[b]	16.2[b]

[a] Dissolved.

[b] Grain dropping or fissures on bending.

[c] – 1.0 mil/year = 2.54×10^{-2} mm/A.

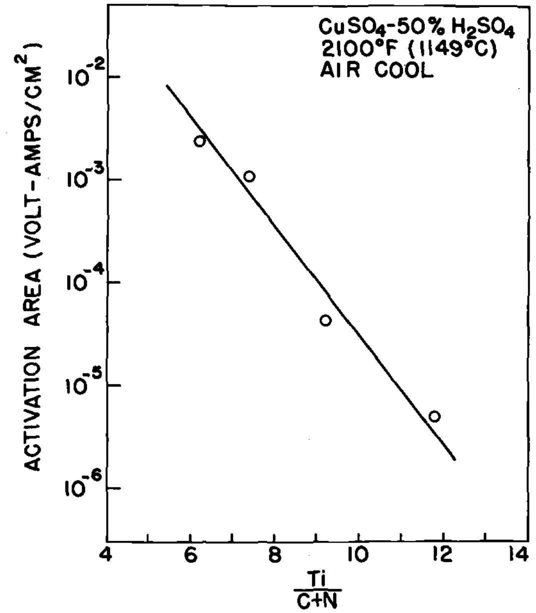

FIG. 6—*Relationship between primary activation area and Ti/C + N ratio in Type 26-1S.*

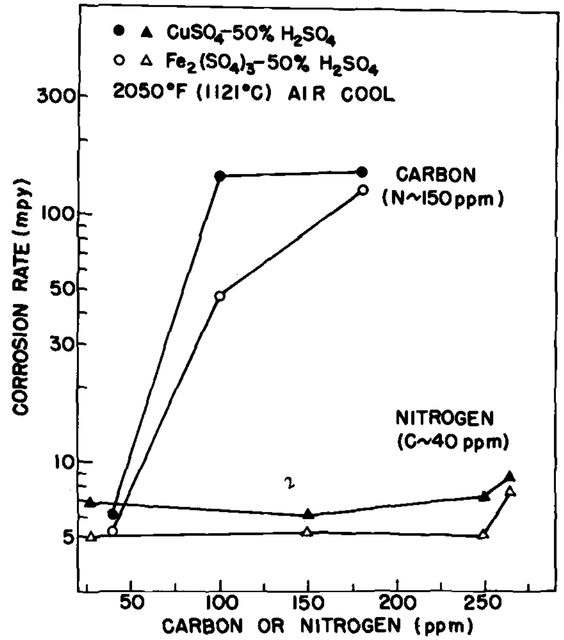

FIG. 7—*Effect of carbon and nitrogen content on the corrosion rate of heat-treated Type 29-4 (1.0 mil/year = 2.5 × 10^{-2} mm/A).*

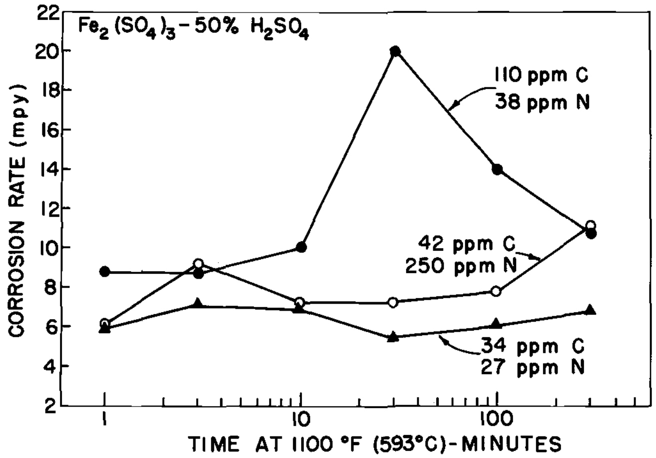

FIG. 8—*Effect of time at 593°C (1100°F) on the corrosion rate of heat-treated (1121°C (2050°F), water quenched) Type 29-4 (1.0 mil/year = 2.5 × 10^{-2} mm/A).*

utilized. For Type 29-4, the carbon and nitrogen levels must be maintained below certain levels, and the tolerance for nitrogen is higher than for carbon [*4*]. Again, the particular chemistry requirement depends on the evaluation test used.

The results obtained with heat-treated specimens illustrate the dependence of a sensitization temperature on chemical composition and thermal history. Figures 3 and 4 show that with Type 26-1S the observed sensitization temperature increases when the Ti/C+N ratio is increased and also when water quenching is employed rather than air cooling or cooling in

TABLE 4—*Corrosion rates (mil/year)*[c] *of heat-treated*[a] *Type 29-4.*

Composition, ppm			Test 1 $CuSO_4$	Test 2 HNO_3	Test 3 $CuSO_4$	Test 4 $Fe_2(SO_4)_3$
C	N	C+N	16% H_2SO_4	HF	50% H_2SO_4	50% H_2SO_4
40	150	190	0.3	3.8	6.1	5.2
100	150	250	0.4[b]	7.9[b]	142.1	47.3[b]
180	160	340	5.3[b]	31.8[b]	151.3	127.1[b]
110	38	148	4.9[b]	30.8[b]	61.6[b]	51.0[b]
34	27	61	0.2	4.2	6.9	5.0
40	150	190	0.3	3.8	6.1	5.2
42	250	292	0.3	3.2	7.3	5.1
45	265	310	0.4	4.7[b]	8.7	7.6[b]

[a] 1121°C (2050°F), 5 min, air cool.
[b] Grain dropping or fissures on bending.
[c] 1.0 mil/year = 2.5 × 10^{-2} mm/A.

vermiculite. The occurrence of an upper sensitization temperature is presumably related to the chemical and thermal conditions which produce a sensitized microstructure. This is the temperature at which significant amounts of carbon and nitrogen are in solution and thus available to form chromium carbides or nitrides on cooling to room temperature. The effect of Ti/C + N ratio is thus a result of both increased stability (that is, slower dissolution kinetics) and increased precipitation kinetics of titanium carbide and titanium nitride as the Ti/C + N ratio increased. The increase in apparent sensitization temperature for water quenching (Fig. 3) is a result of a reduction in the amount of precipitation with a faster cooling rate. The results in Table 3 illustrate that water quenching (contrasted with air cooling) also increased the observed sensitization temperature in Type 29-4. The highest carbon material sensitized to a greater degree than the lower carbon steels, even at 1232°C (2250°F), when water quenched.

The existence of a lower sensitization temperature and the dependence on chemistry was shown for Type 29-4 in Fig. 8. This represents the temperature range where carbon or nitrogen, or both, which has been retained in solution by water quenching from an elevated temperature, precipitates as chromium compounds. The decrease in corrosion rate as the time at temperature increases is a result of chromium rediffusion after precipitation is complete. This removes the chromium gradients which cause intergranular corrosion. A similar effect was noted in Fig. 3 where cooling in vermiculite (as compared to water or air cooling) reduced the corrosion rate. The maximum corrosion rate observed at the lower sensitization temperature is much less than the corrosion rates observed after high-temperature exposure of the same material. This is probably a result of the use of only one temperature, 593°C (1100°F), which may not be the temperature which causes the maximum intergranular corrosion rate. This temperature would depend on the chemical composition, particularly, chromium, molybdenum, carbon, and nitrogen.

The different response of the same material in the four corrosion tests (Tables 1 and 2) could be a result of several phenomena. Some of the tests may selectively attack components of the microstructure that other tests do not. The work of Lula, Lena, and Kiefer [2] and Baumel [7] has shown that nitric acid may attack chromium-depleted regions as well as titanium carbides and nitrides; whereas, a $CuSO_4$-16 percent H_2SO_4 solution apparently only attacks regions depleted in chromium. The susceptibility to intergranular attack in $Fe_2(SO_4)_3$-50 percent H_2SO_4 of high Ti/C + N ratio heats of 26-1S is attributed to the attack of titanium carbides or nitrides by this highly oxidizing solution. The resistance to intergranular corrosion in the other solutions of the same material indicates the absence of a significant amount of chromium-depleted regions.

A second cause for variability between tests is the difference in their ability to detect susceptibility to intergranular attack associated with chromium depletion. Streicher [*14*] has shown that the sensitivity of the test to chromium gradients depends on the sensitivity of the corrosion rate in the media on chromium content. The data in Table 4 demonstrate that the $CuSO_4$-16 percent H_2SO_4 test yields much lower corrosion rates than either the $CuSO_4$-50 percent H_2SO_4 test or the $Fe_2(SO_4)_3$-50 percent H_2SO_4 test. As the absolute corrosion rate decreases (for example, from Test 3 to Test 1), the relative sensitivity to chromium content decreases, and thus the ability to detect susceptibility to intergranular corrosion resulting from chromium depletion also is reduced.

A third observed phenomenon which relates to the relative sensitivity of the tests was shown in Fig. 5. Anodic polarization tests in the test media used for immersion testing revealed a difference in both the active dissolution behavior and the passive dissolution behavior. The activation area in the active region correlated with the corrosion rates in the immersion tests (Fig. 8). The significance of this observation is not understood, and further polarization studies are needed.

Conclusions

The purpose of this study was to investigate the parameters (alloy chemistry, thermal history, and solution chemistry) which determine the susceptibility of two new ferritic stainless steels to intergranular corrosion. The results are relevant to the development of evaluation procedures for these alloys and to the understanding of the causes of intergranular corrosion in ferritic stainless steels. Based on the work described in this study, it can be concluded that:

1. Depending on the alloy chemistry, particularly carbon, nitrogen, and titanium, sensitization can be produced in these alloys by either welding or high-temperature annealing, followed by air cooling. Sensitization can also occur with dual heat treatments; however, the combination of heat treatments required depends very much on chemistry of the material being studied.
2. The most reliable evaluation method, independent of the corrosive media, was bending of the material combined with optical examination for evidence of grain dropping. Corrosion rate in the absence of optical examination was not reliable.
3. For Types 26-1S and 29-4, the severity of the standard tests increased in the following order: $CuSO_4$-16 percent H_2SO_4, HNO_3-HF, $CuSO_4$-50 percent H_2SO_4, and $Fe_2(SO_4)_3$-50 percent H_2SO_4. The significance of the tests with regard to chemistry requirements of the alloys will have to be resolved by correlation with results obtained in actual service environments.
4. The results are consistent with models relating intergranular corrosion in ferritic stainless steels to the presence of regions depleted in chromium.

The attack of high Ti/C + N ratio heats of Type 26-1S in $Fe_2(SO_4)$ is attributed to the direct attack of titanium compounds.

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A. J. Sweet[1]

Detection of Susceptibility of Alloy 26-1S to Intergranular Attack

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ABSTRACT: Alloy 26-1S, a titanium-stabilized ferritic stainless steel, is of commercial interest because of its good as-welded properties, its resistance to chloride stress-corrosion cracking (SCC), and its low cost relative to other alloys having these characteristics. It has been found that understabilization of 26-1S can lead to sensitization and susceptibility to intergranular attack (IGA) in typical chemical industry solutions and to SCC in hot, chloride-bearing water. To ensure that a given batch of Alloy 26-1S is stabilized properly and resistant to sensitization, specimens from each batch should be tested by appropriate acceptance tests. Two suitable acceptance tests were identified (an etch test and an acid corrosion test), and pass/fail criteria were determined.

KEY WORDS: stainless steels, intergranular corrosion, corrosion, stress corrosion, sensitizing, ferritic stainless steels, corrosion tests, stabilization, acceptability, weldments, heat affected zone

Alloy 26-1S (XM-33) is a titanium-stabilized, ferritic stainless steel having a nominal composition of 26 percent chromium, 1 percent molybdenum, and balance iron. The principal advantages of Alloy 26-1S are its good as-welded ductility and corrosion resistance and its resistance to chloride stress-corrosion cracking (SCC). These properties make Alloy 26-1S a good candidate for use where SCC is a problem, such as piping and tubing handling hot, chloride-bearing water. Significantly more expensive materials such as titanium, Alloy 20 Cb-3, and nickel-based alloys are now used to combat SCC under these conditions.

The good post-weld properties of Alloy 26-1S can be impaired if the material is sensitized by welding or other thermal means. Susceptibility to this sensitization can occur if the material is produced understabilized (ratio of Ti/(C + N) too low) or if the material has been contaminated with

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carbon or nitrogen during fabrication. To ensure that a given batch of Alloy 26-1S has the required corrosion resistance it is necessary that a specimen from each batch be subjected to an acceptance test capable of detecting sensitization and insufficient stabilization.

The objectives of this study were to investigate the effects that sensitization has on the corrosion resistance of Alloy 26-1S and to identify suitable acceptance tests and criteria for determining if a given batch of Alloy 26-1S is sensitized or insufficiently stabilized.

Sensitization and Stabilization of Ferritic Stainless Steels

The mechanism of sensitization of ferritic stainless steels has been extensively studied. Recent investigators [*1–7*][2] have shown that sensitization is caused by the formation of chromium-depleted zones along grain boundaries. Their work indicates that certain thermal treatments cause chromium-rich carbides ($M_{23}C_6$) and nitrides (β-Cr_2N) [*5*] to form at grain boundaries. This process significantly lowers the chromium content of the adjacent zone, thereby reducing its corrosion resistance. This zone is then susceptible to preferential corrosion in some environments resulting in intergranular attack (IGA) and the dropping out of grains.

In ferritic stainless steels sensitization is caused in susceptible materials by cooling from temperatures above 930°C (1700°F). Such cooling would occur in weldments and in weld heat-affected zones (HAZ). Sensitization occurs as the material is cooling between 870 and 480°C (1600 and 900°F). The sensitization reaction is too rapid in susceptible steels for even water quenching to suppress it; consequently, welds in this material cannot escape sensitization.

Commercial annealing of ferritic stainless steels such as Types 430 and 446 is performed by holding at 760 to 816°C (1400 to 1500°F) which improves ductility and rediffuses chromium into the chromium-depleted zones. The remaining structure contains chromium carbides and nitrides but not their harmful chromium-depleted zones. However, if the material is welded, the chromium carbides and nitrides dissolve and, upon cooling, reform and create new chromium-depleted zones. If the weld is not given a postweld anneal to rediffuse the chromium, the weld will have poor mechanical and corrosion properties. This problem has limited severely the utility of conventional ferritic stainless steels such as Types 430 and 446.

Two approaches have been used recently to produce ferritic stainless steels with good postweld ductility and corrosion resistance. One approach is to lower the carbon and nitrogen levels to low values as is done with Alloy 29-4 (Fe-29Cr-4Mo) [*8*] and Alloy XM-27 (Fe-26Cr-1Mo) [*9*]. The other approach is to add stabilizers such as titanium or columbium to

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

preferentially combine with, or tie up, the carbon and nitrogen, thus making them unavailable for chromium carbide or nitride formation. The stabilization approach is used for Alloy 26-1S.

The stabilization reaction in Alloy 26-1S occurs at around 930°C (1700°F). Therefore, in adequately stabilized materials a cooling weldment has its carbon and nitrogen tied up before the item cools into the chromium carbide and nitride formation range of 870 to 480°C (1600 to 900°F). A detailed discussion of stabilization temperatures and phases is presented by Pollard [*10*].

Other Causes of IGA in Alloy 26-1S

Sensitization due to the formation of chromium carbides and nitrides is not the only phenomenon that can make Alloy 26-1S susceptible to IGA. It has been long known that ferritic stainless steels adequately stabilized with titanium still suffer IGA of their weldments in hot, concentrated nitric acid [*11*]. This IGA has been reported [*2, 12, 13*] to be caused by the direct dissolution of titanium carbides and nitrides by nitric acid (HNO_3). If these precipitates form a continuous sheath along grain boundaries, then IGA will result from their dissolution.

It has been also shown [*9,14,15*] that properly titanium-stabilized ferritic stainless steels will suffer IGA in solutions such as the ferric sulfate test solution after welding or after certain heat treatments. Demo reports [*15*] that the cause may be a submicroscopic chi-phase similar to the submicroscopic sigma-phase that apparently occurs in Types 316L and 321.

Test Descriptions and Results

Experimental Plan

Attempts were made to produce sensitized coupons by welding sheets from several commercial and laboratory heats of Alloy 26-1S. Welding was chosen as the sensitizing treatment since welding will be the most common, potentially damaging thermal treatment that Alloy 26-1S product will receive after manufacture. The heats used had a variety of stabilization ratios so that welding produced specimens that included badly sensitized, mildly sensitized, and nonsensitized material.

Specimens cut from each welded sheet were then subjected to candidate acceptance tests and to various corrosion tests simulating plant conditions. These simulated service tests included conditions existing in chemical process plants for which Alloy 26-1S would be applied and which would cause IGA or SCC of susceptible materials. Since all of the specimens in a set were cut from the same weld, it was assumed that the specimens from each thickness of plate from a given heat received identical sensitizing treatments.

The intent was to compare the results from specimens exposed to the candidate acceptance tests with identical specimens exposed to the simulated plant solution tests. The acceptance test that best matched the plant solution test results could then be used to screen materials for plant environments.

Materials Used

The materials used in this program came from commercial and laboratory heats made and supplied by Allegheny-Ludlum Steel Corporation. The commerical heats were 63.5-metric tonne (70-ton) heats made by a vacuum refining process. The laboratory heats, 22.7 kg (50 lb), were made in such a way as to include all of the tramp elements present in the commercial heats. The stabilization ratios of the lab heats were varied to allow the study of the effects of understabilization. The material was supplied to us as 5.1-mm (0.200-in.) thick plates some of which we rolled down to 2.5 mm (0.100 in.). Both thicknesses were given stabilizing heat treatments of about 930°C (1700°F) before use in this program. Table 1 lists the ASTM specified chemical limits for Alloy 26-1S and the chemical analyses of the heats used in this program.

Specimen Preparation

The sheets were welded without filler metal using a gas-tungsten-arc (GTA) method. Argon coverage was maintained on front and back surfaces of the plates. Travel speed was about 20 cm/min (8 in./min). Thick plates were welded using about 22 V and 240 amp while for the thinner plates 14 V and 120 amp were used.

Specimens for metallographic evaluation were made by cutting across the weld to allow examination of a full cross section of the weld, HAZ, and base metal. No surface grinding was performed so that the cross section of grain boundaries near the original surface could be studied.

The specimens for the acid corrosion tests were made about 2 cm (0.75 in.) wide by 3.8 cm (1.5 in.) long with the weld parallel to the 2-cm direction. Each specimen contained weld metal, HAZ, and base metal. The specimens were given X80 grit wet belt finishes on all surfaces, which is a standard finish for many acceptance tests. The specimens for the simulated service IGA tests were given an additional metallographic polish on one edge that intersected a weld to facilitate examination for mild IGA. All of the specimens were measured, washed, degreased, and weighed before use.

Specimens for the stress-corrosion tests were made according to the ASTM Method for Evaluating Stress Corrosion Effect Of Wicking-Type

TABLE 1—*ASTM chemical specifications for Alloy 26-1S and chemical analyses of Type 26-1S heats used in this program.*

Heat Code	Stabilization Ratio, Ti/(C + N)	C	N	Ti	Al	Si	Mn	P	S	Cr	Mo	Ni	Cu
ASTM Specifications	7 min	0.06 max	0.04 max	0.20 to 1.00	. . .	0.75 max	0.75 max	0.040 max	0.020 max	25.0 to 27.0	0.75 to 1.50	0.50 max	0.20 max
A	0.09	0.039	0.0156	0.005	0.012	0.13	0.17	0.015	0.011	26.24	1.01	0.18	. . .
B	3.0	0.028	0.015	0.13	0.032	0.23	0.26	0.018	0.015	25.86	1.02	0.19	0.052
C	5.3	0.026	0.014	0.21	0.028	0.23	0.27	0.018	0.014	25.91	1.02	0.18	0.051
D	7.6	0.028	0.014	0.32	0.040	0.25	0.27	0.019	0.015	25.86	1.02	0.18	0.052
E	9.4	0.037	0.015	0.49	0.050	0.25	0.26	0.019	0.015	25.86	1.02	0.18	0.052
F	13.5	0.033	0.015	0.65	0.050	0.25	0.25	0.019	0.015	25.86	1.02	0.18	0.050
G	14.5	0.039	0.0140	0.77	0.44	0.14	0.15	0.007	0.005	26.21	1.02	0.18	. . .
X	7.8	0.03	0.019	0.38	0.02	0.20	0.30	0.025	0.012	26.00	0.97	0.14	0.06
Y	16.6	0.054	0.0098	1.06	0.69	0.16	0.17	0.015	0.011	25.05	0.96	0.18	0.030
Z	20.0	0.057	0.0094	1.33	0.68	0.31	0.25	0.017	0.009	25.85	1.20	0.28	0.038

NOTES—ASTM Specification for Stainless and Heat-Resisting Chromium Steel Plate, Sheet, and Strip (A 176-75).
Heats A through G were 22.7-kg (50-lb) heats.
Heats X through Z were 63.5-metric tonne (70-ton) heats.
Analyses by Allegheny-Ludlum Steel Corp.

Thermal Insulations On Stainless Steel (C 692-71). The specimens were made from strips that were approximately 7.5 by 18 cm (3 by 7 in.) with the weld parallel to the 18 cm direction. The strips were given an X80 grit finish after welding and before bending. The specimens were then bent and stressed to 90 percent of their yield strength. The specimens were dye-penetrant tested after bending and stressing but before testing to ensure that they were initially crack free.

Candidate Acceptance Tests

All of the practices in the ASTM Practice for Detecting Susceptibility to Intergranular Attack in Stainless Steels (A 262-75), several variations, and some new tests were evaluated. The test descriptions and a discussion of the results are given in the following sections.

Sulfuric Acid (H_2SO_4) *Etch Test*—This sulfuric acid etch has been found suitable for metallographic etching of Alloy 26-1S. It was thought that something in the microstructure might correlate with performance in the plant service solutions so it was included as a candidate acceptance test.

Metallographic mounts were made of complete cross sections of welds on sheets from many of the heats under study. These were polished metallographically and etched electrolytically in 5 percent by volume H_2SO_4 in water. A voltage of 2.0 V was used which resulted in a current density of about 1.5 A/cm^2.

Evaluations of the specimens were performed on a metallograph at magnifications between ×100 and ×800. The observations from these evaluations appear in Table 2. In addition to the comments listed in this table, the microstructures of all the materials contained large numbers of fine precipitates that were probably titanium carbides and nitrides.

Ditching occurred at the grain boundaries on many of the specimens. The worst cases involved ditching in the base metal with grain dropping occurring in the HAZ and weld. Moderate cases suffered ditching in the HAZ and weld. The best cases experienced no ditching and had step structures. An example of a ditched specimen appears in Fig. 1. Generally, ditching increased as the stabilization ratio decreased.

Some specimens that primarily had step structures had a few small patches of ditching near the surface in the HAZ and weld. Slight contamination of the surface before or during welding probably was responsible for this ditching.

Oxalic Acid Etch Test—The oxalic acid etch test is described in ASTM A 262-75 as Practice A. It was developed by Streicher [*16*] as a rapid means to detect sensitization in austenitic stainless steels. It detects the presence of chromium carbides which for austenitic stainless steels normally means that the material is sensitized.

Streicher [*7*] recommends that since the oxalic test detects the presence

TABLE 2—*Results of evaluation of welded specimens of Alloy 26-1S by a sulfuric acid etch*[a] *and by the oxalic acid etch test.*[b]

Heat	Stabilization Ratio	Thickness, mm	Sulfuric Acid Etch	Oxalic Acid Etch
B	3.0	2.5	...	severe ditching + GD[c] in weld + HAZ; ditching in base
C	5.3	2.5	...	severe ditching + GD in weld + HAZ
D	7.6	2.5	...	severe ditching + GD in weld + HAZ (Fig. 2)
E	9.4	2.5	...	random ditching in HAZ + weld in interior (Fig. 3)
F	13.5	2.5	...	step structure (Fig. 3)
G	14.5	2.5	...	step structure
B	3.0	5.1	severe ditching in base, HAZ, weld; GD in HAZ + weld	severe ditching in base, HAZ, weld; GD in HAZ + weld
C	5.3	5.1	severe ditching in HAZ + weld; a few small GD	ditching + GD in weld + HAZ only
D	7.6	5.1	ditching in HAZ + weld; a few small GD (Fig. 1)	ditching in weld
E	9.4	5.1	ditching at surface in weld and HAZ	step structure
F	13.5	5.1	ditching in HAZ at surface	...
X	7.8	2.5	ditching near surface in HAZ + weld; scattered ditching in HAZ in interior	step structure
Y	16.6	2.8	small area of ditching in weld at surface	...
Z	20.0	2.6	step structure	...
Z	20.0	4.3	ditching at surface in HAZ	step structure

[a] Electrolytic etch in 5 percent H_2SO_4.

[b] ASTM A 262, Practice A.

[c] GD = grain dropping and HAZ = heat-affected zone.

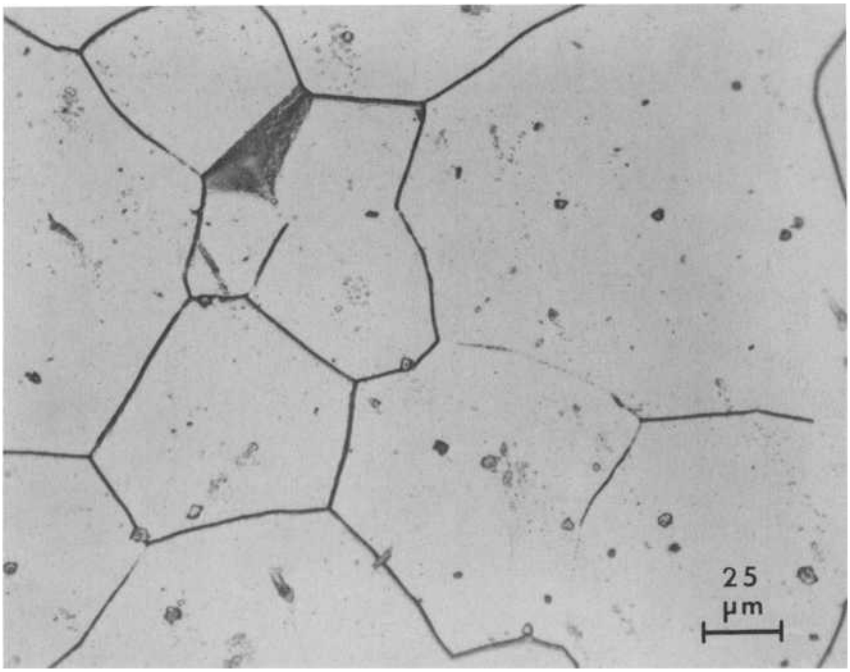

FIG. 1—*Sulfuric acid etch of the 5.1-mm-thick specimen of Heat D showing ditched grain boundaries and dropped grain.*

of chromium carbides, it should not be used on ferritic stainless steels such as Types 430 and 446. These alloys, when properly annealed, contain many chromium carbides at their grain boundaries, but chromium has been rediffused into the chromium-depleted zones restoring their corrosion resistance. Therefore, the test would detect these carbides and unjustly "fail" properly-annealed, corrosion-resistant Types 430 and 446. This reasoning does not apply to stabilized ferritic stainless steels since they should not have chromium carbides in the mill-annealed, as-welded, as stress-relieved, or any other condition. The presence of chromium carbides would indicate understabilization or sensitization. Therefore, the oxalic test was considered a viable candidate for use with stabilized ferritic stainless steels.

The oxalic test consists of etching a specimen in an aqueous 10 percent oxalic acid solution at 1 A/cm^2 for 90 s. The presence of chromium carbides at grain boundaries is revealed by preferential ditching at the grain boundaries. In the absence of chromium carbides, the grain boundaries appear as steps. Photomicrographs of these structures in austenitic material appear in ASTM A 262-75. For this program full cross sections of welds from many of the heats were etched. Evaluations were performed on a metallograph at magnifications up to ×800. The results of these evaluations appear in Table 2.

In general, the grain boundaries of heats with low stabilization ratios were heavily ditched and in some cases, actual grain dropping occurred. The worst specimens suffered ditching in the base metal, HAZ, and weld. The moderate cases had the ditching limited to the HAZ and weld. The best specimens, which came from high stabilization ratio heats, had step structures with no ditching. No scattered spots of ditching occurred near the surface as was the case for the sulfuric etching. Heavy etch pitting occurred on all of the specimens which may have obscured small sections of ditching. A photomicrograph of a severely sensitized specimen with massive grain dropping is shown in Fig. 2. Examples of mild ditching and a step structure are portrayed in Fig. 3.

Ferric Sulfate Test (*Streicher Test*)—This test is used as an acceptance test for austenitic stainless steels (ASTM A 262-75, Practice B) and nickel-based alloys, ASTM Method of Detecting Susceptibility to Intergranular Attack in Wrought Nickel-Rich, Chromium-Bearing Alloys (G 28-72). It was developed by Streicher [*17*] as a faster, less expensive alternative to the

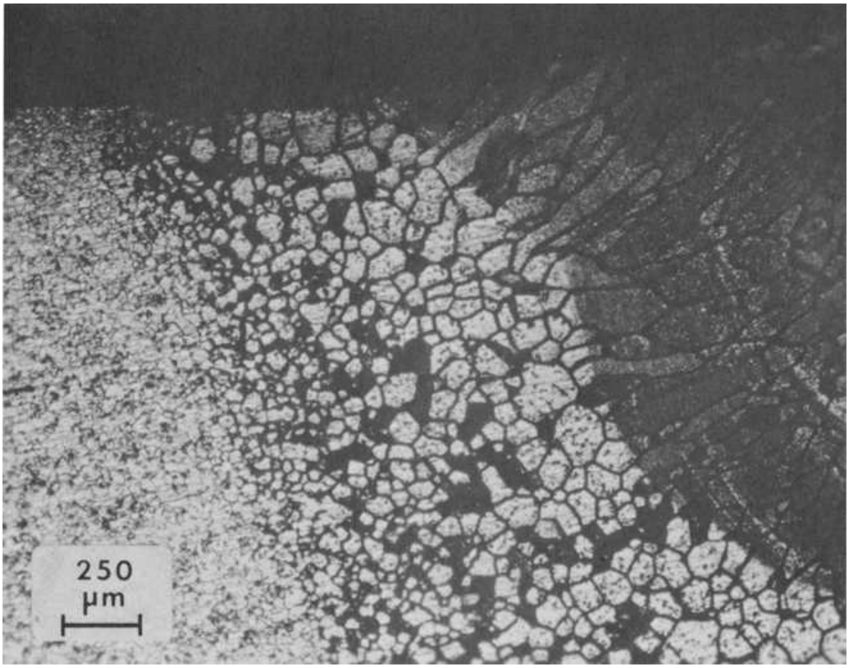

FIG. 2—*Oxalic acid etch of 2.5-mm-thick specimen of Heat D showing ditching and grain dropping in HAZ* (center) *and weld* (right).

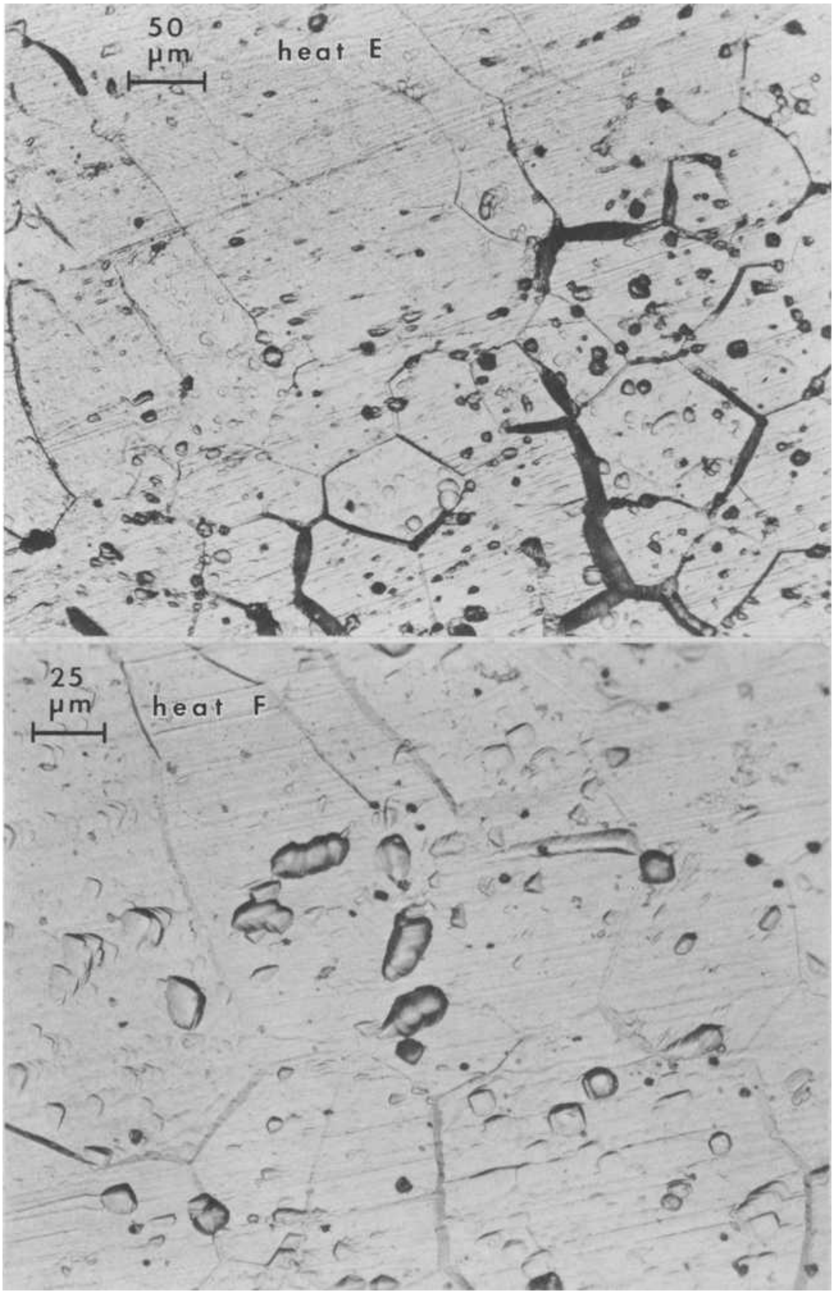

FIG. 3—*Oxalic acid etch of 2.5-mm-thick specimens of Heat E showing ditching in weld* (upper left) *and HAZ* (lower right) *and Heat F showing step structure in weld* (upper left) *and HAZ* (lower right).

nitric acid test for the detection of chromium carbide sensitization in austenitic stainless steels. As discussed previously, phenomena other than chromium carbide sensitization can cause IGA of titanium-stabilized ferritic stainless steels in the test. Streicher has shown [*18*] that this test also detects a submicroscopic sigma-phase in Type 321, a titanium-stabilized austenitic stainless steel. Streicher has recommended the ferric sulfate test for use with ferritic Types 430 and 446 [*7*] and Airco has recommended [*9*] its use for evaluating welded or unwelded E-Brite 26-1 (XM-27).

The test for austenitic stainless steels consists of exposing a specimen to boiling 50 percent H_2SO_4 containing 41.7 g/litre hydrated ferric sulfate $[Fe_2(SO_4)_3 \cdot XH_2O]$ for 120 h. These conditions were used in this program. One specimen was tested per flask. Evaluation was performed by calculation of corrosion rates and by microscopic examination. The results of this evaluation are given in Table 3.

The weld metal and HAZ of all the specimens tested suffered grain dropping. The severity of the attack decreased with increasing stabilization ratio, but significant attack occurred even at the highest ratios.

Nitric Acid Test (*Huey Test*) —The nitric acid test is described in ASTM A 262-75, Practice C. It is used widely as an acceptance test for the detection of chromium carbide type sensitization in certain austenitic stainless steels. It is not usually used for Types 316L or 317L unless they are in-

TABLE 3—*Results of evaluations of welded Alloy 26-1S specimens by the ferric sulfate*[a] *and nitric acid tests.*[b]

Heat	Stabilization Ratio	Thickness, mm	Ferric Sulfate Corrosion Rate, mm/year	Nitric Acid Corrosion Rate, mm/year
A	0.09	2.5	29	1.2
B	3.0	5.1	8.0	1.6
C	5.3	5.1	10	4.4
D	7.6	5.1	2.9	5.0
E	9.4	5.1	0.73	3.6
F	13.5	5.1	0.43	0.79
G	14.5	5.2	0.40	0.24[c]
X	7.8	2.5	0.70	4.2
Y	16.6	2.8	0.73[c]	0.24
Z	20.0	2.6	1.2	1.7
Y	16.6	4.7	1.2	...
Z	20.0	4.3	1.3	3.0

NOTE—Grain dropping in the weld and HAZ occurred on all specimens in both tests.
1 mm/year = 39.4 mil/year = 0.0033 in./month.

[a] ASTM A 262, Practice B.

[b] ASTM A 262, Practice C.

[c] Also slight grain dropping in base metal.

tended for nitric acid service since it detects submicroscopic sigma-phase in these alloys [*19,20*]. This phase is harmless in plant environments except nitric acid (HNO_3) [*20*].

The nitric acid test is not particularly useful for unstabilized ferritic stainless steels because it is much less sensitive to sensitization than is the ferric sulfate test [*7*]. Also it has not been used for titanium-stabilized ferritic stainless steels, since it preferentially attacks the titanium carbonitrides. The test was included in this program to confirm that it is not appropriate for titanium-stabilized ferritic stainless steels and to serve as a simulated service test since HNO_3 acid solutions are extensively used in the chemical process industry.

The test consists of exposing the test specimen to boiling 65 percent by weight HNO_3 for a number of periods totaling 240 h. For this program one 72-h period, followed by one 96-h period, followed by another 72-h period were used. Fresh acid was used for each period. The tests were conducted in a multispecimen tester designed by DeLong [*21*]. The evaluation of the specimens was done by the calculation of corrosion rates and by microscopic observations. The results of these evaluations are given in Table 3.

The nitric acid test, like the ferric sulfate test, caused grain dropping in the weld and HAZ of all the specimens tested. However, the severity of the attack increased with increasing stabilization ratios at low ratios and decreased with increasing ratios at high ratios.

Nitric-Hydrofluoric Acid (*HF*) *Test* (*Warren Test*)—The nitric-hydrofluoric acid test is described in ASTM A 262-75, Practice D. This test was studied by Warren [*22*] for use with Types 316, 316L, 317, and 317L. These alloys may contain a submicroscopic sigma-phase which causes them to fail the nitric acid test even though the alloys are acceptable for most plant applications.

The use of the nitric-hydrofluoric acid test for austenitic stainless steels consists of exposing the test specimen and an annealed specimen from the same batch to a solution of 10 percent by weight HNO_3 plus 3 percent by weight HF at 70°C for two 2-h periods. Evaluation is performed by calculating the ratio of corrosion rates. A ratio of test specimen rate to annealed specimen rate greater than 1.5 indicates sensitization. A ratio is used because the general corrosion rate varies sharply with the alloy content. A specimen of Type 316L with 16.0 percent chromium may corrode at a high rate even though no IGA occurred. A specimen with 18.0 percent chromium with many grains dropped may corrode at a low rate. Therefore to separate the effects of general corrosion and IGA the ratio method is recommended. Work preliminary to this study indicated that ratios may not be applicable for Alloy 26-1S, since, in many cases, the ratio was found to be less than 1.0 and occasionally was as low as 0.3. Apparently Alloy 26-1S weld metal corrodes at a much lower general corrosion rate than the base metal. The possibility exists that significant grain dropping could occur on the welded specimen, and the ratio would still be below 1.0. Therefore for this program only a welded specimen was tested and ratios were not used.

The test is somewhat inconvenient to run since it involves the use of HF, which is considerably more hazardous than the other acids. Also, it is more difficult to control accurately the test temperature of 70°C in plastic equipment than it is to control the temperature of the boiling solutions in glass apparatus. The test does have the advantage of being faster than the other hot acid corrosion tests.

The specimens were exposed for a total of at least 8 h and in some cases 28 h. This additional time was used because initial results indicated that the two 2-h periods could only detect severe sensitization. Evaluation was done by microscopic evaluation. Corrosion rates were also calculated but care must be used in interpreting these rates until the effect of varying chromium levels and the presence of weld metal is determined. The results of the evaluation are given in Table 4.

Examination of the results shows that, for both the 4 and 8-h exposures, increasing stabilization ratios resulted in decreasing grain dropping. The alloy had to have higher stabilization ratios to escape IGA in the 8-h exposure than the 4-h exposure. Also at a given stabilization ratio more grains were dropped in 8 h than in 4 h. Although not given in Table 4, it was found that extending the time up to 28 h provided no additional information.

Cupric Bend Test (*Modified Straus Test*)—There have been several variations of the original sulfuric acid-cupric sulfate test. The variations differ in the acid concentration used, in the presence or absence of metallic copper, and in the location of this copper relative to the specimen. The variation covered in this section is described in ASTM A 262-75, Practice E. There is general agreement in the literature [*2,11-13,23*] that the various acidified cupric sulfate tests detect chromium carbide and nitride type sensitization in titanium-stabilized ferritic stainless steels and do not detect titanium carbides or nitrides or sigma-phase.

The specimens for these tests were made similar to those used for the other acceptance tests except that their length was about 7.5 cm (3 in.) instead of 3.8 cm. Where possible three identical specimens were made of each heat and thickness. One of these specimens was not exposed to any acid test but was used as a control specimen during evaluation. The second and third specimens were exposed to the test solution for 24 h (as specified in Practice E) and 72 h, respectively. The test solution was made according to Practice E which results in a solution of 15.7 percent by weight H_2SO_4 and 5.7 percent cupric sulfate ($CuSO_4$) [*18*]. Metallic copper chips or turnings are packed around the specimen, and the solution is used at boiling for the test period. The specimens are evaluated by bending them

TABLE 4—*Results of evaluation of welded specimens of Alloy 26-1S in the nitric-HF test (ASTM A 262, Practice D).*

Heat	Stabilization Ratio	Thickness, mm	4-h Exposure		8-h Exposure	
			mm/year	Grain Dropping	mm/year	Grain Dropping
A	0.09	2.5	35	yes: weld + HAZ	. . .	. . .
B	3.0	2.5	43	yes: weld + HAZ	. . .	. . .
C	5.3	2.5	5.3	yes: HAZ	6.3	yes: weld + HAZ
D	7.6	2.5	4.5	none	4.8	yes: weld + HAZ
E	9.4	2.5	2.5	none	2.5	none
F	13.5	2.5	2.7	none	2.9	none
B	3.0	5.1	5.1	2 GD[a]	6.9	yes: weld + HAZ
C	5.3	5.1	4.0	none	4.1	yes: HAZ
D	7.6	5.1	2.6[b]	none	2.5	no GD
			4.5[b]	none	3.6	1 GD
			3.5[b]	none	3.2	2 GD
E	9.4	5.1	2.3	none	2.2	none
F	13.5	5.1	3.3	none	2.9	none
G	14.5	5.2	2.2	none	2.5	none
X	7.8	2.5	2.4	none	2.3	none
Y	16.6	2.8	6.2	none	6.2	none
Z	20.0	2.6	3.7	none	4.1	none
Y	16.6	4.7	4.8	none	5.3	none
Z	20.0	4.3	3.0	none	3.3	none

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[a] GD = grains dropped.

[b] Triplicate tests.

around a mandrel with a small radius. Any IGA will lead to fissures visible under a microscope.

The control, 24, and 72-h specimens were all bent according to Practice E and examined at magnifications of at least ×40. The control specimen was used to determine if any cracking or fissuring occurred solely because of mechanical weakness of the material. The results of these tests are given in Table 5.

A few of the thinner materials developed some fissures away from the welded area. These fissures occurred on both the control and acid-exposed specimens so it was considered a mechanical problem, not a corrosion problem. This fissuring did not appear related to stabilization ratio so it was not likely a function of sensitization.

Some of the thicker control specimens with low stabilization ratios, and the associated acid-exposed specimens, cracked into two pieces. Other materials that were sufficiently ductile to allow the control specimen to be bent still broke into two pieces after exposure to the acid. This occurred with both high and low stabilization ratio heats. Because of the ductility problems it was impossible to clearly determine the effect of sensitization on IGA for some specimens.

Modified Cupric Test—The modified cupric test is the second variation of the acidified cupric sulfate test evaluated in this program. Its primary difference is that it uses 50 percent H_2SO_4 instead of 15.7 percent and is run for 120 h instead of 24 h. It is not yet a part of any standardized test specification.

The test apparatus is the same as for ASTM A 262-75, Practice B, plus an additional glass cradle containing a 0.6 by 2.5 by 5-cm piece of clean copper. The test solution is made according to the following steps.

1. Add several boiling chips to a clean, empty 1000-ml Erlenmeyer flask.
2. Add 71.4-g reagent grade $CuSO_4 \cdot 5H_2O$ to the flask.
3. Add 400.0 ml of distilled water to the flask.
4. *Slowly* add 236.0 ml reagent grade 95.0 to 98.0 percent by weight H_2SO_4 to the flask.
5. Put glass cradle containing the copper into the solution.

After bringing the solution to a vigorous boil, the test specimen held in a glass cradle is put into the solution and kept there for 120 h.

The modified cupric test was developed by Streicher [*18*] to study the corrosion of Type 321 stainless steel. He determined that the submicroscopic sigma that caused IGA in the nitric acid test and ferric sulfate test did not cause IGA in this cupric sulfate test. Apparently the cupric sulfate test was selective only to chromium carbide and nitride sensitization. Herbsleb and Schwaab [*13*] reported its use in studies of columbium- and titanium-stabilized ferritic stainless steels. A proposal for this test to be considered as an acceptance test for Alloy 26-1S was presented by Pollock, Sweet, and Collins [*24*].

TABLE 5—*Results of evaluation of welded specimens of Alloy 26-1S in the cupric bend test (ASTM A 262, Practice E).*

Heat	Stabilization Ratio	Thickness, mm	0-h Bend Observations	24-h Observations	72-h Observations
B	3.0	2.5	good bend	cracked in weld	cracked in weld
C	5.3	2.5	good bend	cracked in weld	cracked in weld
D	7.6	2.5	few fissures away from weld	cracked in weld	cracked in weld
E	9.4	2.5	few fissures away from weld	few fissures away from weld	few fissures away from weld
F	13.5	2.5	good bend	good bend	good bend
B	3.0	5.1	cracked in weld	cracked in weld	cracked in weld
C	5.3	5.1	cracked in weld	cracked in weld	cracked in weld
D	7.6	5.1	cracked in weld	cracked in weld	cracked in weld
E	9.4	5.1	good bend	good bend	good bend
F	13.5	5.1	good bend	cracked in weld	cracked in weld
X	7.8	2.5	...	1 good bend 1 IGA fissurizing in weld + HAZ	2 good bends
Y	16.6	2.8	...	cracked in weld	2 good bends
Y	16.6	4.7	...	good bend	good bend

For this program the specimens were tested according to the foregoing instructions. They were evaluated by microscopic examination at magnifications of at least ×40 and by weight loss measurements. In addition those specimens that were marginal or had no grain dropping were bent as in the cupric bend test (Practice E) and again examined. The results of these tests are given in Table 6. An example of mild grain dropping is pictured in Fig. 4.

Examination of the results indicates that corrosion, whether monitored by corrosion rates or by microscopic examination, increased with decreasing stabilization ratios. The corrosion consisted of IGA resulting in grain dropping in the weld and HAZ. Of the laboratory heats only those with stabilization ratios of 9.4 or greater were immune. None of the specimens from the three commercial heats suffered grain dropping.

The attempt to bend the specimens that did not drop grains was hindered by their short length. A few good bends did result indicating a complete lack of IGA on those specimens. Both the thick and thin specimens of Heat E developed a few fissures indicating a slight amount of IGA.

Simulated Service Tests—Intergranular Corrosion

A group of test solutions and conditions were selected that represent typical environments in chemical industry plants in which Alloy 26-1S would be probably used and which would likely cause IGA of susceptible material.

As mentioned previously, the specimens used in these tests were welded and had an ×80 grit finish on all surfaces except that one of the edges that intersected the weld was metallographically polished.

The tests in boiling solutions were conducted in the equipment specified for ASTM A 262-75, Practice B (1-litre Erlenmeyer with Allihn condenser), with about 600 ml of solution. The flasks were heated by hot plates. The tests at temperatures below boiling were conducted in large glass test tubes fitted with stoppers. Water-filled glass crook tubes acted as a seal between the test solution and the atmosphere. The test tubes were heated by placing them in constant temperature water baths.

Most of the specimens were removed and examined for attack after 336, 672, 1700, and 3336 h. Specimens with significant grain dropping were terminated early. The solutions were changed periodically depending on the amount of corrosion that occurred.

Evaluation of the specimens was done by weight loss measurements and by microscopic examination at magnifications between ×12 and ×1000 depending on the amount of attack. In some cases metallographic mounts were made of cross sections of the specimens to measure the depth of IGA.

A description of the individual tests and their results are given in the

TABLE 6—*Results of evaluation of welded specimens of Alloy 26-1S in the modified cupric test.*[a]

Heat	Stabilization Ratio	Thickness, mm	Modified Cupric Test		Modified Cupric Bend Observations
			mm/year	Grain Dropping	
A	0.09	2.5	19	yes: weld + HAZ	. . .
B	3.0	2.5	8.0	yes: weld + HAZ	. . .
C	5.3	2.5	6.1	yes: weld + HAZ	. . .
D	7.6	2.5	0.94	yes: weld + HAZ	. . .
E	9.4	2.5	0.19	none	some fissuring in weld + HAZ
F	13.5	2.5	0.16	none	good bend
B	3.0	5.1	2.5	yes: weld + HAZ	. . .
C	5.3	5.1	1.4	yes: weld + HAZ	. . .
D	7.6	5.1	0.62	yes: weld + HAZ	. . .
E	9.4	5.1	0.19	none	some spotty IGA in weld
F	13.5	5.1	0.16	none	cracked in weld
G	14.5	5.2	0.19	none	. . .
X	7.8	2.5	0.20	none	good bend
Y	16.6	2.8	0.29	none	good bend
Z	20.0	2.6	0.23	none	. . .
Y	16.6	4.7	0.24	none	. . .
Z	20.0	4.3	0.22	none	. . .

[a] Boiling 50 percent H_2SO_4 + $CuSO_4$ + Cu for 120 h.

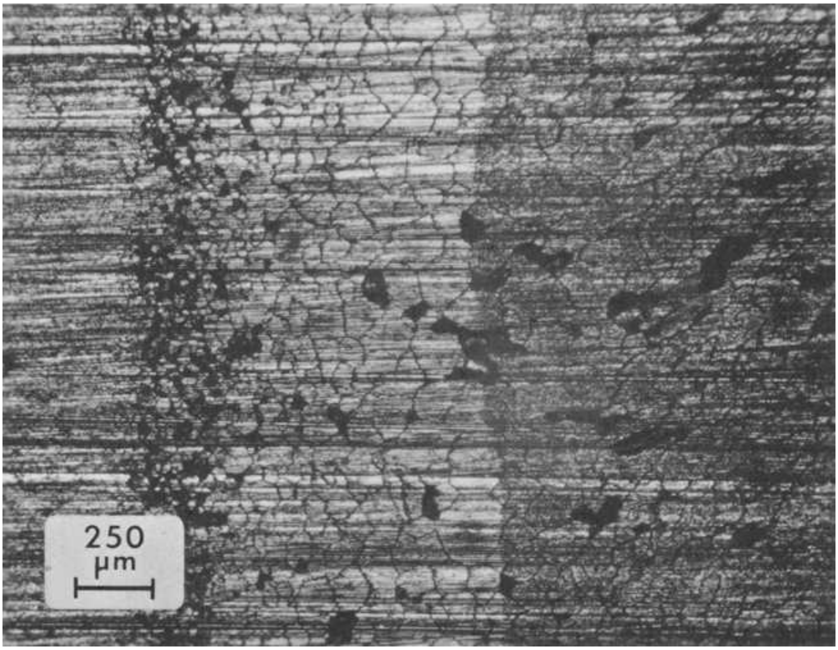


FIG. 4—*Specimen of 5.1-mm-thick Heat C after exposure to modified cupric test showing grain dropping in HAZ and weld (Original magnification ×40).*

following sections. The test data are presented in Tables 7 through 9. The nomenclature used describing the intensity of grain dropping is:

Few—1 to 10 grains dropped per coupon (about 20 cm^2).

Some—More than 10 grains dropped per coupon but weld still basically intact.

Severe—Significant portions of weld or HAZ gone.

Boiling 45 Percent Formic Acid—This solution was shown by Warren [*20*] to cause intergranular etching of sensitized Type 316 stainless steel. Formic acid environments of all concentrations at many temperatures are likely candidates for the application of Alloy 26-1S; therefore, this solution appeared to be a good candidate for this program.

The results of the tests in boiling 45 percent formic are given in Table 7 along with the results from the boiling 0.5 percent H_2SO_4 tests. The following observations and conclusions were made:

1. The weld on Heat X appeared to be contaminated. One part of the weld was completely immune to IGA while another area suffered significant grain dropping.
2. The severity of grain dropping decreased with increasing stabilization ratio. The specimens with the highest ratios were immune to IGA.

TABLE 7—*Results of tests of welded specimens of Alloy 26-1S in boiling 45 percent formic acid and boiling 0.5 percent H_2SO_4.*

			Boiling 45% Formic Acid		Boiling 0.5% H_2SO_4	
Heat	Stabilization Ratio	Thickness, mm	Total Exposure, h	Comments	Total Exposure, h	Comments
A	0.09	2.5	336	severe GD[a]	336	severe GD
B	3.0	2.5	336	severe GD	336	severe GD
C	5.3	2.5	336	severe GD	336	severe GD
D	7.6	2.5	336	severe GD	336	some GD
E	9.4	2.5	1704	2 GD at 336 h, many at 1704	1704	some GD at 672 h and at 1704
F	13.5	2.5	3336	2 corners out at 3336 h	3336	few corners out at 1704 h (Fig. 5, 6)
B	3.0	5.1	336	severe GD	672	few GD at 336 h, many at 672
C	5.3	5.1	336	severe GD	1704	few GD at 336 h, many at 1704
D	7.6	5.1	1671	slight GD at 336 h, severe at 1671	1671	few GD at 672 h, some at 1671
E	9.4	5.1	3335	no GD	3335	few corners out at 3335 h
F	13.5	5.1	3335	no GD	3335	no GD
G	14.5	5.2	3336	no GD	3336	no GD
X	7.8	2.5	1671	one patch of localized GD	3335	few corners out at 1671 h
Y	16.6	2.8	3335	no GD	3335	few corners out at 3335 h
Z	20.0	2.6	3336	no GD	3336	few corners out at 1704 h
Y	16.6	4.7	3336	no GD	3336	few corners out at 1704 h
Z	20.0	4.3	3336	no GD	3336	few corners out at 1704 h

[a] GD = grain dropping.

3. Typical general corrosion rates were 0.025 mm/year (1.0 mil/year) meaning an average penetration of about 0.010 mm (0.0004 in.) during the course of the test.

Boiling 0.5 Percent H_2SO_4—This solution was shown by Warren [*20*] to cause significant grain dropping from sensitized Type 316 stainless steel specimens. The results of these tests are given in Table 7. The following observations and conclusions were made:

1. The severity of grain dropping decreased with increasing stabilization ratio.

2. Typical general corrosion rates were 0.01 mm/year (0.4 mil/year) meaning a penetration of about 0.0038 mm (0.00015 in.) during the test exposure.

3. Many of the best specimens suffered some dropping of a few grain corners. One of these specimens, the 2.5-mm-thick Heat F was studied metallographically to determine the seriousness of the attack. Figure 5 shows the surface of the polished edge of the specimen with its IGA and a few very small grains dropped. Figure 6 shows this surface in cross section. Metallographic measurements showed that the grain boundary attack was

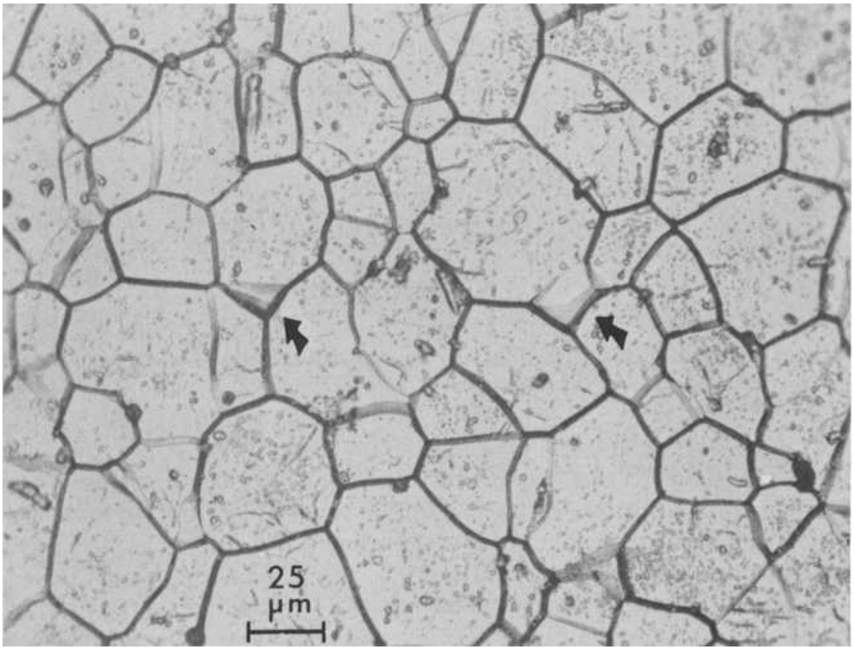
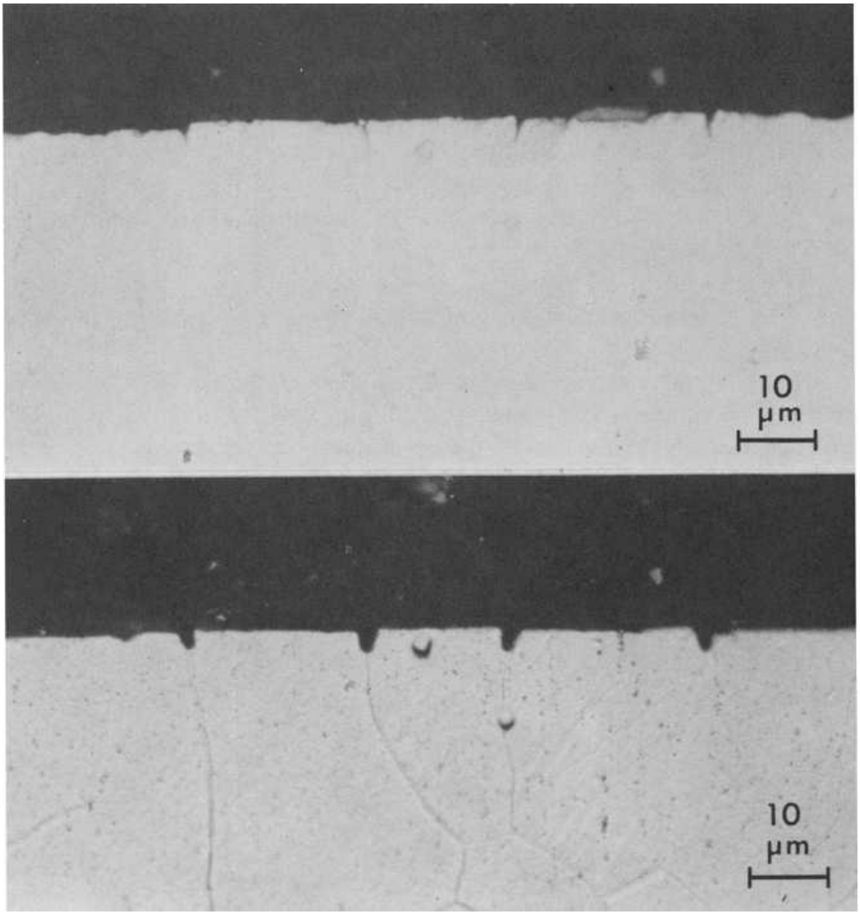


FIG. 5—*Polished edge of the 2.5-mm-thick specimen of Heat F in the HAZ after 3336 h in boiling 0.5 percent* H_2SO_4 *showing grain boundary attack and small grains dropped out* (arrows).



Top: Unetched.
Bottom: Etched.

FIG. 6—*Cross section of polished edge of the 2.5-mm-thick specimen of Heat F in the HAZ after 3336 h in boiling 0.5 percent H_2SO_4. Grain boundary penetration was measured as 0.0038 mm (0.00015 in.).*

0.0038 mm (0.00015 in.) deep. When added to the general corrosion the total penetration during the test was 0.0076 mm (0.00030 in.). This corresponds to a total penetration rate of less than 0.020 mm (0.0008 in.) per year which was considered insignificant.

Boiling 20 Percent by Weight Acetic Acid—This solution was shown by Warren [*20*] to cause significant IGA of sensitized Type 316 stainless steel. Acetic acid of all strengths and at many temperatures is a likely environment for which 26-1S may be applied; therefore, it seemed appropriate as a test solution for this program.

The test data are presented in Table 8. Examination of these data indicates:

1. Boiling 20 percent acetic acid is not as severe as boiling 45 percent formic acid or 0.5 percent H_2SO_4 in causing IGA of susceptible Alloy 26-1S.
2. Material with low stabilization ratios suffered some grain dropping.
3. The general corrosion rate in this solution was about 0.00038 mm/year (0.015 mil/year).

72 Percent by Weight H_2SO_4 Plus 1.5 Percent by Weight HNO_3 at 40°C—This solution at 60°C was shown by Auld [25] to cause significant grain dropping of mildly and severely sensitized Type 304 stainless steel and is representative of some environments used in the chemical process industry. The 40°C temperature was chosen to allow these tests to be run in the same test equipment as the other 40°C tests and to keep the general corrosion rate at a minimum.

The test data are presented in Table 8. Examination of the test data reveals:

1. The severity of grain dropping decreased with increasing stabilization ratio.
2. The general corrosion rate in this solution was about 0.005 mm/year (0.2 mil/year).

5 Percent by Weight H_2SO_4 at 40°C—This environment was chosen to study the effect of sensitization of Alloy 26-1S in a second H_2SO_4 environment.

The test data given in Table 9 indicate that no grain dropping occurred on the heats with high stabilization ratio. However, Heat A, with its 0.09 ratio, suffered a mixture of severe, active general corrosion with no IGA in one area and little or no general corrosion but severe IGA in another, smaller area. Perhaps the IGA occurred in a crevice formed between the specimen and its cradle. It also appears significant that the specimen with the most severe sensitization corroded actively. This observation indicates that sensitization in ferritic stainlesses may also damage general corrosion resistance. It is also interesting that the part of the specimen that corroded actively did not suffer IGA. Only the passively corroded surface dropped grains. This result is similar to the findings of Streicher [7] concerning the corrosion of ferritic stainlesses in H_2SO_4.

5 Percent by Weight H_2SO_4 + 2 Percent HF at 40°C—This solution was chosen to determine what effect the fluoride ion would have on IGA of Alloy 26-1S. The solution was too aggressive and actively corroded all of the specimens at a high rate, about 100 mm/year (4000 mil/year).

The tests and their results are given in Table 9. It is again noteworthy that Heat A, which was sensitized severely, did not suffer IGA while undergoing active corrosion.

Boiling 5 Percent by Weight Sodium Chloride (NaCl) at pH = 3 with Hydrochloric Acid (HCl)—This environment was chosen to determine if

TABLE 8—*Results of tests of welded specimens of Alloy 26-1S in boiling 20 percent acetic acid and 40°C 72 percent H_2SO_4 + 1.5 percent HNO_3.*

			Boiling 20% Acetic Acid		40°C 72% H_2SO_4 + 1.5% HNO_3	
Heat	Stabilization Ratio	Thickness, mm	Total Exposure, h	Comments	Total Exposure, h	Comments
A	0.09	2.5	336	severe GD[a]	1708	few GD at 340 h, severe at 1708
B	3.0	2.5	672	few GD at 336 h and at 672	672	few GD at 336 h and at 672
C	5.3	2.5	1704	few GD at 672 h and at 1704	672	few GD at 336 h and at 672
D	7.6	2.5	1704	few GD at 672 h and at 1704	672	few GD at 336 h and at 672
E	9.4	2.5	3336	no GD	3336	few GD at 1704 h and at 3336
F	13.5	2.5	3336	no GD	3336	no GD
B	3.0	5.1	3336	few GD at 336 h and at 3336	1708	few GD at 353 h and at 1708
C	5.3	5.1	3336	no GD	1708	few GD at 353 h and at 1708
D	7.6	5.1	3335	no GD	1708	few GD at 676 h and at 1708
E	9.4	5.1	3335	no GD	3340	no GD
F	13.5	5.1	3335	no GD	3340	no GD
G	14.5	5.2	3336	no GD	3340	no GD
X	7.8	2.5	3335	no GD	3340	few GD at 1709 h
Y	16.6	2.8	3335	no GD	3340	no GD
Z	20.0	2.6	3336	no GD	3340	no GD
Y	16.6	4.7	3336	no GD	3340	no GD
Z	20.0	4.3	3336	no GD	3340	no GD

[a] GD = grain dropping.

TABLE 9—*Results of tests of welded specimens of Alloy 26-1S in 40°C 5 percent H_2SO_4, 40°C 5 percent H_2SO_4 + 2 percent HF, and Boiling 5 percent NaCl.*

			40°C 5% H_2SO_4		40°C 5% H_2SO_4 + 2% HF		Boiling 5% NaCl, pH = 3 with HCl	
Heat	Stabilization Ratio	Thickness, mm	Total Exposure, h	Comments	Total Exposure, h	Comments	Total Exposure, h	Comments
A	0.09	2.5	24	severe general corrosion; no GD except one spot that has many GD in weld + HAZ	24	no GD[a,b]	3336	no GD; slight pitting, intergranular SCC down center of weld after 672 h, eventually specimens broke in two
G	14.5	5.2	3340	no GD	24	no GD[a,b]	3336	no GD; a few pits
Z	20.0	2.6	3340	no GD	24	no GD[a,b]	3336	no GD, a few pits
Y	16.6	4.7	3340	no GD	24	no GD[a,b,]	3336	no GD; a few pits
Z	20.0	4.3	3340	no GD	24	no GD[a,b]	3336	no GD or pits

[a] GD = grain dropping.

[b] Severe general corrosion: about 100 mm/year.

chloride-bearing cooling waters would cause IGA of sensitized Alloy 26-1S. The specific tests and their results are given in Table 9. None of the specimens suffered any detectable conventional IGA. However, the Heat A specimen cracked down the center of its weld. Microscopic examination of the fracture showed it to be purely intergranular. None of the weld grain boundaries except those associated with the crack showed any attack. Apparently the specimen suffered intergranular SCC.

Simulated Service Tests—Stress Corrosion Cracking

The primary reason for the existence of Alloy 26-1S is its inherent resistance to chloride SCC. However, work by Streicher on Types 430, 446, and 29-4 [*8,26*] indicates that sensitization of ferritic stainless steels damages their resistance to SCC. Tests were conducted in this program to determine the effect of varying levels of sensitization of Alloy 26-1S on its resistance to SCC.

The test chosen for this study was the wick test which was developed by Dana and DeLong [*27,28*] for the evaluation of pipe insulation materials for their tendency to cause SCC of stainless steel. ASTM C 692-71 was eventually prepared to standardize this test. Warren [*29*] used the test to study the effect of chloride ion concentration and metal temperature on the SCC of Type 304 stainless steel. His work showed that using a neutral wick, a 1500-ppm chloride ion solution, and a metal temperature of 100°C provided a rapid test realistically simulating conditions normally found in condensers cooled with chloride-bearing water.

The test procedure for the evaluation of alloys consists of following ASTM C 692-71, Paragraphs 5, 6, 7, 9, 10.2, 10.3 and all figures. The neutral wick, 10.2-cm (4-in.) glass tube and 1500-ppm chloride ion solution are used as described in Paragraph 6.2. For this program one thin welded specimen (2.5 mm) each of Heats B, C, D, E, and F was exposed for 30 days. Those specimens that were not obviously cracked were then dye penetrant tested to ensure that they were still crack-free.

The specimens of Heats B and C were cracked severely in the weld area (Fig. 7). Metallographic examination revealed that the cracking was intergranular (Fig. 8) and was limited to the weld metal and HAZ. The specimens of Heats D, E, and F were not cracked. These results mean that welded material of Heats B and C probably would crack in service. Heats D, E, and F may be resistant, but longer test times and several duplicate specimens would have to be run to be certain.

These tests show that sensitized Alloy 26-1S even when partially stabilized will fail by SCC in the as-welded condition. Therefore suitable acceptance tests should be conducted on materials intended for use in chloride-bearing cooling waters regardless of the process stream.

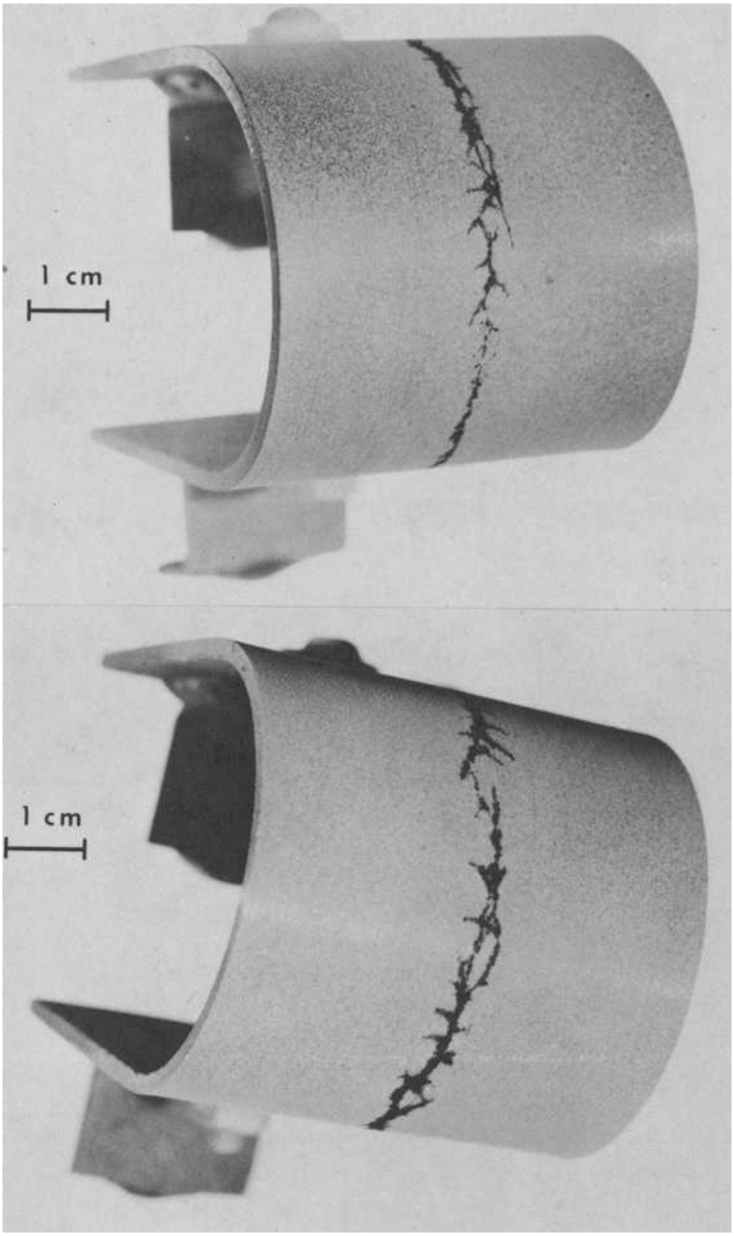
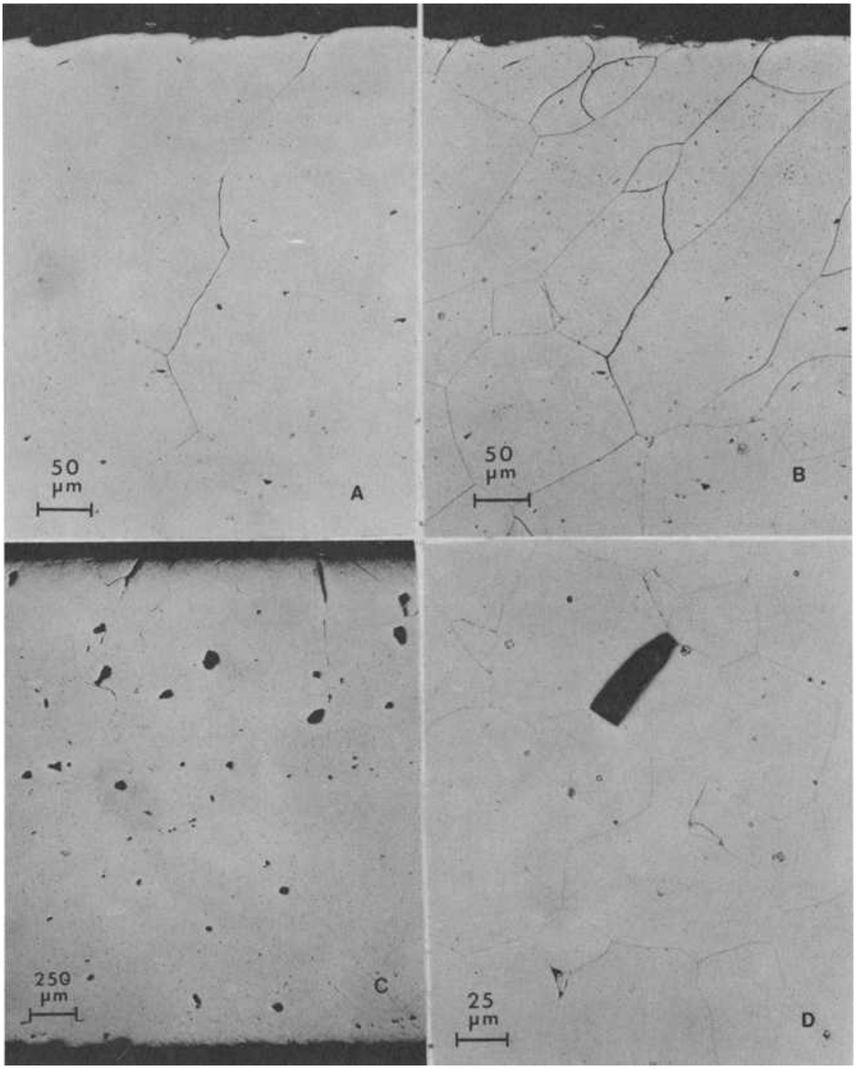


FIG. 7—*U-bends of 2.5-mm-thick sheet from Heat B* (top) *and Heat C* (bottom) *after testing in wick test for 30 days and after dye-penetrant testing.*



A. Unetched showing crack in weld near HAZ.
B. Same as A but etched.
C. Unetched showing holes left by loose grains that fell out during polishing.
D. Unetched showing fine cracks in HAZ that surround virtually every grain.

FIG. 8—*Intergranular SCC on cross sections of thin Heat C wick test specimen.*

Pitting Tests

Work by several investigators [*6,8,30*] has shown that sensitization damages the resistance of ferritic stainless steels to pitting corrosion. These data are of particular concern since an expected major use of Alloy 26-1S is as tubing in condensers cooled with chloride-bearing cooling water.

To determine the effect of sensitization of Alloy 26-1S on its resistance to pitting, a series of 10 percent ferric chloride tests were conducted. This test method has been widely used for the evaluation of the relative pitting resistance of stainless steels.

For this test program the specimens were welded and prepared in the same manner as those exposed to the candidate acceptance tests. No crevices were put on the specimens. The tests were conducted in large, glass test tubes containing the coupons and 150 ml of 10 percent ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$). The coupons were exposed at room temperature (24 to 30°C) for over six months. Microscopic evaluations were performed at 24, 649, and 4561 h. The heats tested and the results are given in Table 10.

TABLE 10—*Results of pitting tests of welded specimens of Alloy 26-1S in 10 percent* $FeCl_3 \cdot 6H_2O$ *under ambient conditions with no crevices.*

Heat	Stabilization Ratio	Thickness, mm	Total Exposure Time, h	Observations
A	0.09	2.5	24	severe IGA in weld only, many grains dropped
G	14.5	5.2	4561	several small, randomly scattered pits; no IGA
Z	20.0	2.6	4561	severe pitting in base metal; no IGA
Y	16.6	4.7	649	three large pits in base metal; no IGA
Z	20.0	4.3	4561	several small, randomly scattered pits; no IGA

The work reported here was initiated before the availability of most of the understabilized heats. Therefore the information obtained is sketchy. However, the following conclusions can be drawn:

1. Nonsensitized Alloy 26-1S is susceptible to conventional pitting in the ambient 10 percent ferric chloride test without crevices.
2. Severe weld sensitization causes conventional IGA in the test similar to that caused by acid tests.
3. Too few tests were conducted in this program to conclude that sensitization diminishes the pitting resistance of 26-1S. A test more closely simulating plant pitting conditions is needed to study this matter further.

Comparison of Acceptance Tests with Simulated Service Tests

The results presented in Tables 2 through 10 and the stress corrosion results were studied to determine which of the candidate acceptance tests could be relied upon to predict plant performance. A summary of these data is presented in Table 11.

TABLE 11—*Comparison of the results of the candidate acceptance tests and the simulated plant service tests.*

Specimen			Candidate Acceptance Tests									Simulated Service Tests					
					Nitric-HF Test		Cupric Bend Test										
Heat	Stabilization Ratio	Thickness, mm	Ferric Sulfate Test	Nitric Acid Test	4 h	8 h	24 h	72 h	Modified Cupric Test	Sulfuric Acid Etch	Oxalic Acid Etch	Boil 45% Formic	Boil 0.5% H_2SO_4	40°C 72% H_2SO_4 and 1.5% HNO_3	Boil 20% Acetic	40°C 5% H_2SO_4	SCC Wick Test
A	0.09	2.5	X	X	X	...	...	...	X	...	...	S	S	S	S	S	...
B	3.0	2.5	...	...	X	...	X	X	X	...	X	S	S	S	S	...	S
C	5.3	2.5	...	...	X	X	X	X	X	...	X	S	S	S	S	...	S
D	7.6	2.5	...	...	P	X	X	X	X	...	X	S	S	S	S	...	R
E	9.4	2.5	...	...	P	P	P	P	P	...	X	S	S	S	R	...	R
F	13.5	2.5	...	...	P	P	P	P	P	...	P	R	R	R	R	...	R
B	3.0	5.1	X	X	P[a]	X	X	X	X	X	X	S	S	S	S	...	...
C	5.3	5.1	X	X	P	X	X	X	X	X	X	S	S	S	R	...	...
D	7.6	5.1	X	X	3P	3P[a]	X	X	X	X	X	S	S	S	R	...	...
E	9.4	5.1	X	X	P	P	P	P	P	P	P	R	R	R	R	...	...
F	13.5	5.1	X	X	P	P	X	X	P	P	...	R	R	R	R	...	...
G	14.5	5.2	X	X	P	P	...	...	P	...	...	R	R	R	R	R	...
X	7.8	2.5	X	X	P	P	1P,1X	2P	P	X	P	M	R	S	R	...	...
Y	16.6	2.8	X	X	P	P	X	2P	P	P	...	R	R	R	R	...	...
Z	20.0	2.6	X	X	P	P	...	...	P	P	...	R	R	R	R	R	...
Y	16.6	4.7	X	...	P	P	P	P	P	...	...	R	R	R	R	R	...
Z	20.0	4.3	X	X	P	P	...	...	P	P	P	R	R	R	R	R	...

NOTE-P = Passed: no grain dropping visible at × 40 or no significant ditching in etch tests.
X = Failed: grain dropping visible at × 40 or significant ditching after etch test.
M = Mixed: probably due to local contamination.
R = Resistant to IGA or SCC.
S = Susceptible to IGA or SCC.

[a] Had 1 or 2 grains dropped that would not likely be visible at × 40 by average observer.

The 5 percent H_2SO_4 + 2 percent HF IGA tests, the 5 percent NaCl IGA tests, and the $FeCl_3$ pitting tests seemed to contribute little to the selection of acceptance tests so they were omitted from Table 11. The results from Heat X were erratic and inconsistent with results from the other heats; therefore, data from Heat X were not used in conclusions concerning the suitability of the various acceptance tests.

The sulfuric and oxalic acid etches seemed to correlate very well with the simulated plant solution tests if the material with significant ditching was considered as failed and step structures were passed. The etch tests were neither too weak (allow susceptible material to pass) nor too strong (fail good material). For practical testing the oxalic test appears better than the sulfuric test because the ditched boundaries visually contrast with the good boundaries better in the oxalic test than they do in the sulfuric test.

The ferric sulfate and nitric acid tests caused grain dropping from all the specimens tested, including those that were resistant to IGA in the plant solution tests. These two solutions apparently detected a grain boundary condition other than chromium carbides and nitrides. This condition may be submicroscopic sigma- or chi-phase. In any case this condition did not cause IGA in the simulated plant solution tests and therefore is considered harmless except in some aggressive, oxidizing solutions.

If the acceptance criterion is a lack of grain dropping then neither test is of any value. If a corrosion rate criterion is used then the nitric acid test is of no value since the corrosion rates (Table 3) did not correlate with the results of the simulated service tests. Looking at the ferric sulfate data (Table 3) it appears that a maximum allowable rate of 1.5 mm/year (0.005 in./month) would pass the good heats and reject the poor heats, except thin Heat E. However, various combinations of chromium level, possible sigma- and chi-phases, chromium carbide sensitization, and ratios of weld metal to base metal would likely thwart the use of ferric sulfate corrosion rates for accepting as-welded Alloy 26-1S.

The nitric acid test also served as a simulated plant solution test. The weldments of all the specimens suffered IGA in the nitric acid tests; therefore, as-welded, titanium-stabilized 26-1S cannot be used in hot, concentrated nitric acid regardless of stabilization ratio. However, material that is not welded or material that has been welded and then cold worked and annealed may be suitable for nitric service. More test work is needed before any such recommendations can be made.

The 4-h nitric-hydrofluoric acid test is clearly too weak to predict performance in our plant environments. The thick specimens of Heats B, C, and D and the thin specimens of Heats D and E did not drop grains in the 4-h test but were susceptible to IGA in at least two of the plant solutions.

The 8-h nitric-hydrofluoric acid test is better than the 4-h version but is still not good enough. Thick Heat D and thin Heat E passed the 8-h test but suffered IGA in the plant solutions. Also some of those that failed the 8-h test did not fail badly and may have been labelled as passed by other observers.

Figure 9 shows specimens from thin Heat D that were exposed to the 8-h nitric-hydrofluoric acid test, the modified cupric test, and boiling 45 percent formic acid. The formic specimen demonstrates that this material is highly susceptible to failure in service, and this is shown adequately by the cupric specimen. However, the nitric-hydrofluoric test specimen only dropped a few grains indicating its weakness in detecting susceptibility of Alloy 26-1S to IGA.

A look at the 8-h corrosion rates (Table 4) indicates that they could not be used as acceptance criteria. Thin Heat Y had a corrosion rate of 6.2 mm/year and did not drop grains in the nitric-hydrofluoric test or the simulated service tests. Thick Heat C corroded at 4.1 mm/year and suffered grain dropping in the nitric-hydrofluoric test and the service tests. A maximum allowable corrosion rate that would pass good thin Heat Y would also pass poor thick Heat C. As mentioned previously a ratio of the corrosion rates of the test specimen to an annealed control specimen from the same batch does not work for Alloy 26-1S because weld metal apparently corrodes at a lower rate than annealed material. This frequently yields ratios less than 1.0 even though grain dropping occurs.

The cupric bend test performed better than the nitric-hydrofluoric test. It allowed only one specimen, thin Heat E, to pass that was susceptible to IGA in the plant solutions. However, since this is a bend test it is inevitable that brittleness problems become confused with IGA. Nonsensitized heats that are brittle for reasons such as section thickness or weld defects will fail this test. This brittleness problem appears to have happened with thick Heat F which was resistant to IGA in the simulated service tests but cracked during bending. Extending the test exposure to 72 h did not affect the test results.

The modified cupric test, using a no-grain-dropped acceptance criterion, matched results with the simulated service tests (see Fig. 9) except for thin Heat E which passed the test but suffered IGA in three solutions. As with the ferric sulfate test the corrosion rates also matched the service tests. A maximum acceptable rate of 0.30 or 0.45 mm/year (0.0010 or 0.0015 in./month) would sort the good heats from the poor heats except again for thin Heat E. A corrosion rate criterion would not be as risky here as it would with the ferric sulfate test since no grain dropping occurred on the good specimens in the cupric test and more specimens were tested. Nonetheless, round-robin tests and more experience with other heats are needed before a corrosion rate criterion can be recommended.

Thin Heat E was mildly susceptible to IGA in three of the simulated service tests but did not fail the cupric bend test or the modified cupric test. Failure did occur in both etch tests. This heat is probably right on the borderline of adequate stabilization. Apparently the etch tests are more sensitive to mild sensitization than the corrosion tests. Also this result indi-

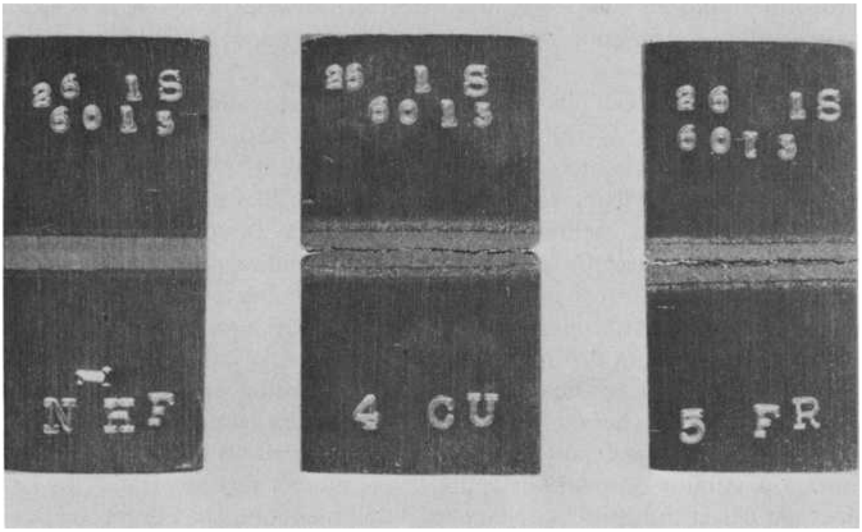


FIG. 9—*Welded specimens of 2.5-mm-thick Heat D after exposure to nitric-HF test for 8 h* (left), *modified cupric test for 120 h* (center), *and boiling 45 percent formic acid for 3336 h* (right).

cates that the use of the etch tests or corrosion tests allows no margin of safety. With 26-1S a small amount of sensitization barely noticed in the acceptance test is sufficient to cause IGA in some services.

Conclusions

1. Welding of understabilized Alloy 26-1S makes the alloy susceptible to IGA in a variety of environments in which Alloy 26-1S will likely be exposed in chemical industry plants. This susceptibility is probably caused by the formation of chromium carbides and nitrides at the grain boundaries in the weld and HAZ.
2. Welding of understabilized 26-1S makes the alloy susceptible to intergranular SCC under conditions expected in heat exchangers and other equipment involving hot, chloride-bearing water. This susceptibility to SCC probably also is caused by the formation of chromium carbides and nitrides.
3. Weldments of Alloy 26-1S, even if properly stabilized, may be susceptible to IGA in some aggressive, oxidizing solutions. Boiling 65 percent HNO_3 and boiling 50 percent H_2SO_4 + Fe^{+3}, both highly oxidizing solutions, cause IGA on properly stabilized weldments, but a solution of 72 percent H_2SO_4 + 1.5 percent HNO_3 at 40°C does not. This effect is caused apparently by the presence of a submicroscopic intermetallic compound, perhaps chi- or sigma-phase, or some other grain boundary condition that is harmless in the simulated plant solutions.
4. Heats of Alloy 26-1S with stabilization ratios greater than 10.0 are

probably stabilized adequately and will resist sensitization. ASTM specifications allow a minimum ratio of 7.0 which is too low to ensure adequate stabilization.

5. Material that exhibits a step structure in the oxalic acid test (ASTM A 262-75, Practice A) will be resistant to SCC and IGA in most plant solutions. However, material with a step structure may still be susceptible to IGA in some oxidizing solutions since this test does not detect the grain boundary condition mentioned in Conclusion 3. Material with a ditch structure may be susceptible to SCC or IGA depending on the extent of the ditching and the corrosivity of the plant environment. This test has the added advantage of showing whether the sensitization is limited to surface grains or extends into the interior.

6. The modified cupric test is the best corrosion acceptance test for Alloy 26-1S if the criterion for passing is a complete lack of dropped grains visible at ×40 magnification. A few grains dropped on the specimen indicates a possibility of eventual failure in the more severe services. This test does not detect the grain boundary condition mentioned in Conclusion 3.

7. The cupric bend test (ASTM A 262-75, Practice E) has the same sensitivity as the modified cupric test just mentioned. However, since it is a bend test, brittleness problems cannot be separated from corrosion resistance problems and could confuse test conclusions. This test also does not detect the grain boundary condition that causes IGA in some oxidizing solutions.

8. The nitric-hydrofluoric acid test (ASTM A 262-75, Practice D) even when used for 8 h is less sensitive to sensitization than the cupric sulfate tests regardless of the criteria used for deciding passing. Material passing this test could still be susceptible to failure in some plant solutions. If used for 4 h it is essentially worthless.

9. The nitric acid test (ASTM A 262-75, Practice C) and ferric sulfate test (Practice B) are not suitable as acceptance tests for applications involving as-welded material in nonoxidizing solutions because they would cause failure of good material as well as poor material. Both solutions detect a grain boundary condition which is detrimental only in oxidizing plant environments. The ferric sulfate test may be appropriate for acceptance testing of material that is not going to be used as-welded in service.

10. Severe sensitization of Alloy 26-1S reduces its ability to remain passive in some solutions.

11. Sensitized Alloy 26-1S is not susceptible to IGA while undergoing active corrosion.

Recommendations

1. All Alloys 26-1S intended for use in plant environments should pass a suitable acceptance test before use. This recommendation is not only for

material intended for handling corrosive process streams but also for material that will be exposed to conditions likely to cause SCC of austenitic stainless steels.

2. To ensure that a given specimen of Alloy 26-1S is completely free of sensitization, the oxalic acid etch test (ASTM A 262-75, Practice A) may be used. If the plant equipment will be used as-welded then the specimen should be welded in the same manner. The etched surface should include a full cross section of the weld, HAZ, and base metal. The criteria should be:

Step Structure: Accept for use in most plant solutions for which Alloy 26-1S has adequate pitting and general corrosion resistance except certain aggressive, oxidizing solutions.

Grain Dropping: Reject for most uses, including those applications involving hot, chloride-bearing water or submit to corrosion acceptance test.

Ditching: It should be assumed that each ditched grain boundary is susceptible to preferential attack in many plant solutions. Minor ditching near the surface should be considered acceptable for most applications. Ditching at interior grains is more serious and such specimens should be rejected or submitted to a corrosion acceptance test.

3. The modified cupric test (50 percent H_2SO_4 + $CuSO_4$ + Cu at boiling for 120 h) is the best available hot acid corrosion acceptance test. If the plant equipment will be used as-welded, then the specimen should be welded in the same manner. The criteria should be:

Specimens that drop no grains visible at ×40 magnification should be accepted and will resist IGA and SCC in most plant environments.

Specimens exhibiting grain dropping visible at ×40 should be rejected.

4. Welded Alloy 26-1S should not be used in environments that have been shown to cause IGA on as-welded, properly stabilized 26-1S. Before using Alloy 26-1S in oxidizing solutions that have corrosion potentials greater than +0.1 V versus SCE, as-welded test specimens of properly-stabilized 26-1S should be shown to resist IGA in the prospective plant environment.

5. To obtain adequate resistance to corrosion Alloy 26-1S should be provided with a stabilization ratio of at least 10.0 which is greater than the 7.0 allowed by ASTM specifications.

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Intergranular Corrosion in 12 Percent Chromium Ferritic Stainless Steels

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ABSTRACT: Intergranular corrosion of Types 409, 405, and 410 stainless steels was evaluated in the heat treated and welded condition. Standard ASTM Method A 262 corrosion tests are too severe for 11 to 13 percent chromium steels, and two modified tests were developed: 65 percent nitric acid at 49°C (140°F) and 50 percent sulfuric acid-cupric sulfate at 49°C (140°F). Type 409, a titanium stabilized ferritic steel, shows intergranular corrosion in nitric acid but is immune in the cupric sulfate test. Type 405 with a duplex structure shows intergranular corrosion in both tests. Type 410 with a martensitic structure does not exhibit intergranular corrosion. The behavior of these steels is explained based on their microstructure.

KEY WORDS: stainless steels, intergranular corrosion, chromium stainless steels, ferritic stainless steels, corrosion tests

Intergranular corrosion in ferritic stainless steels has been reported in the literature as early as 1933 [*1*].[2] The steels used in the earlier studies [*2-4*] were not completely ferritic and when heated at the sensitizing temperatures formed some austenite which transformed to martensite upon cooling to room temperature. For this reason intergranular corrosion was ascribed to the formation of carbon-rich austenite which becomes supersaturated with carbon during cooling. Later studies demonstrated, however [*5*], that austenite was not necessary and that chromium carbides precipitating at the grain boundaries during cooling from temperatures above 930°C (1700°F) in a completely ferritic structure can also produce intergranular corrosion. Electron diffraction studies were used to identify the grain boundary phase [*6*] as chromium rich carbides ($M_{23}C_6$) and possibly an iron-rich nitride. Titanium addition of about six times the combined carbon and

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nitrogen can prevent intergranular corrosion provided the testing solution is not strongly oxidizing [*7*]. Columbium about eight times the carbon and nitrogen content prevents intergranular corrosion even under highly oxidizing conditions.

Intergranular corrosion is prevented in austenitic stainless steels by lowering the carbon and nitrogen contents. In ferritic stainless steels, the maximum allowable carbon and nitrogen contents required to prevent the occurrence of intergranular corrosion increases with increasing chromium and molybdenum contents [*8*]. The required levels in 18 percent chromium ferritic stainless steels cannot be achieved using commercially available melting techniques [*8*]. The higher allowable carbon and nitrogen levels in 26 percent chromium stainless steels ($<$100-ppm carbon and $<$125-ppm nitrogen) can be achieved using available vacuum melting techniques. The addition of titanium or columbium to 26 percent chromium stainless steels with low carbon and nitrogen levels provides additional insurance against the occurrence of intergranular corrosion.

The influence of martensite formation on intergranular corrosion of 17 percent chromium ferritic steels has been investigated by Baumel [*10*]. He found that since austenite formed at high temperature has a higher carbon content than high temperature ferrite there is less of a tendency to precipitate intergranular carbides from carbon supersaturated ferrite during cooling and less intergranular corrosion in nitric acid (HNO_3). Of the two 17 chromium steels which Baumel investigated, the steel that formed 10 percent austenite at high temperature showed considerably more intergranular corrosion than the steel that formed 50 percent austenite.

A corrosion study of a martensitic 13 percent chromium steel with 0.44 percent carbon [*9*] shows that the lowest weight losses in nitric or acetic acids were in the 1016°C (1860°F) oil quenched condition while tempering at 566°C (1050°F) increases the losses. The higher losses in HNO_3 are attributed to general precipitation of chromium carbides during tempering rather than grain boundary precipitation.

The intergranular corrosion of the 11 to 13 percent chromium ferritic stainless steels has not been investigated up to this time because until recently these steels were not used frequently in the welded condition and were applied only in mildly corrosive environments.

The development of Type 409, a ferritic steel containing 11 percent chromium and 0.5 percent titanium, has increased considerably the industrial use of the 11 to 13 percent chromium steels and strengthened the confidence in applying these grades to more demanding corrosion conditions. While extensive field experience with Type 409 in automotive exhaust systems and other applications does not reveal any cases of intergranular corrosion, it is felt, nevertheless, that a study of intergranular corrosion of Type 409 and other 11 to 13 percent chromium steels is opportune. Type 410, a martensitic steel, and Type 405, a steel with a duplex austenitic-ferritic structure at high temperature, have been added to the study to gain a complete picture of intergranular corrosion of the 11 to 13 percent chromium steels. Types 405 and 409 are used in industrial equipment in the welded condition, and a comparative assessment of their resistance to intergranular corrosion is considered important.

Materials

All the materials used in this study were taken from production heats. Heats A and B were melted in the basic oxygen furnace and are representative of the current Types 409 and 405 composition and processing. Heat C was made in the electric arc furnace. All the materials were received in the mill annealed condition in sheet form 0.061 to 0.073 in. thick.

The composition of the steels investigated is shown in Table 1.

The specimens for corrosion testing and metallographic examination were prepared as follows:

(*a*) TIG welded.

(*b*) Heat treated to simulate heat-affected-zone (HAZ) condition:

1. anneal at 982°C (1800°F) 5 min, air cool.
2. anneal at 1093°C (2000°F) 5 min, air cool.
3. anneal at 1204°C (2200°F) 5 min, air cool.

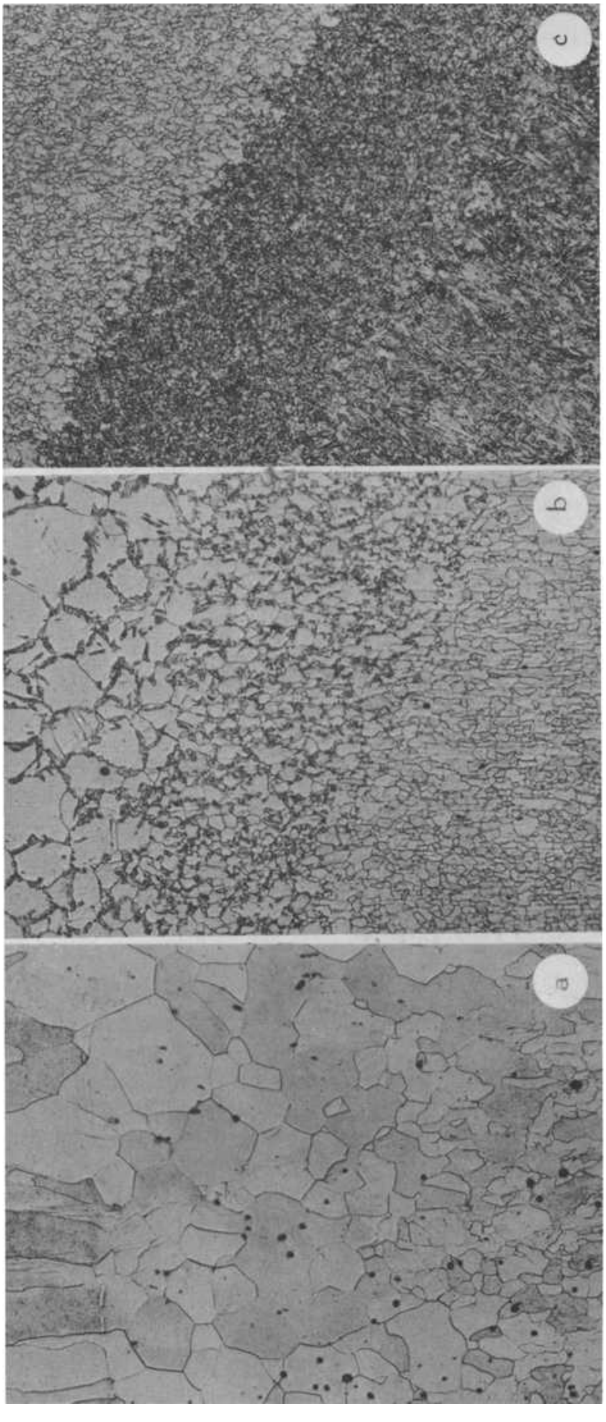
Metallographic Examination

Metallographic examination of the welded and heat treated specimens revealed as expected that the structure of these heats was as follows: Type 409: completely ferritic; Type 405: duplex austenitic-ferritic at high temperature, the austenite transforming to martensite on cooling to room temperature; and Type 410: completely martensitic. This is illustrated in Fig. 1 showing the microstructure of the TIG welds of the three materials. All these heats exhibited considerable coarsening in the high-temperature heat treatments as well as in the weld and HAZ. Coarsening was more pronounced in the heats with a completely ferritic structure. Pronounced surface decarburization took place in Types 405 and 410 especially in the 1204°C (2200°F) heat treatment.

Optical microscopy examination of grain boundaries of the welded and heat treated specimens revealed intergranular precipitates in the HAZ of TIG welded specimens and 1093°C (2000°F) and especially 1204°C (2200°F) heat treated specimens of Type 409. The 982°C (1800°F) annealed specimens showed, however, no grain boundary carbides. Figure 2 shows the microstructure of Type 409 (*a*) in the HAZ of the TIG weld and (*b*) in the 1204°C (2200°F) heat treated material, both with grain boundary precipitates. It is assumed that this precipitate is titanium carbide based on the work done by Baumel [*11*] on 17 chromium steels with

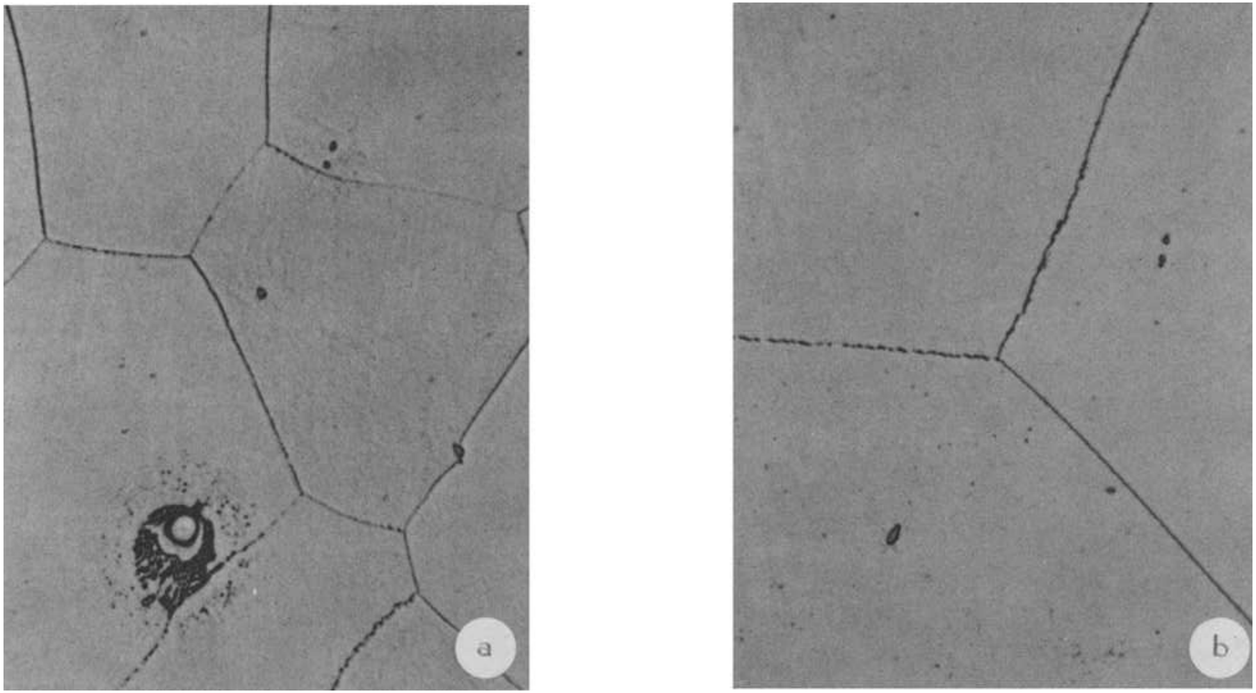
TABLE 1—*Composition of 11 to 13 percent chromium steels.*

Heat No.	Type	C	Si	Mn	S	P	Cr	Ti	Ti/C	Al	Mo	N
A	409	0.042	0.29	0.16	0.01	0.037	11.0	0.46	11	...	...	...
B	405	0.046	0.095	0.17	0.01	0.033	13.56	0.006	...	0.20	0.061	0.024
C	410	0.15	0.35	0.40	0.004	0.024	12.42	0.008	...	0.009	...	...



(*a*) Heat A (×100).
(*b*) Heat B (×100).
(*c*) Heat C (×100).

FIG. 1—*The microstructure of TIG welds of Types 409, 405, and 410.*



(*a*) HAZ of TIG weld (×750).
(*b*) 1204°C (2200°F), 5 min air cool (×750).

FIG. 2—*The microstructure of Type 409 showing intergranular precipitation.*

titanium. Type 405 heat treated at 1093°C (2000°F) and 1204°C (2200°F) shows pronounced broadening of ferrite/ferrite grain boundaries, but no precipitates can be found. The presence of substantial carbide precipitation was not substantiated even with the use of electron microscope thin foil techniques. The completely martensitic structure of Type 410 heat treated at 982 to 1204°C (1800 to 2200°F) or in the weld and HAZ shows no evidence of intergranular carbide precipitation.

Corrosion Tests

An attempt was made to evaluate the susceptibility to intergranular corrosion of the welded and heat treated material using the ASTM Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels (A 262-75) tests. The concentration and temperatures used in these tests which were developed for higher chromium steels proved to be too severe for the 11 to 13 chromium steels, and experiments were made with modifications that included lower testing temperatures, lower concentrations, and shorter exposure times.

Nitric Acid Test

Specimens of welded Type 409 stainless steel which were exposed to boiling 65 percent HNO_3 according to ASTM A 262, Practice C, suffered general corrosion. The test temperature was lowered to 49°C (120°F), and general corrosion was significantly reduced. After three 48-h periods, intergranular corrosion was difficult to discern. A test temperature of 60°C (140°F) was selected for all subsequent tests. The test time was reduced to three 48-h periods.

Cupric Sulfate Test

Specimens of welded Type 409 stainless steel were exposed to ASTM A 262, Practice E, boiling 6 weight percent cupric sulfate ($CuSO_4$)-16 weight percent sulfuric acid (H_2SO_4). The specimens spontaneously activated almost immediately after exposure to this test solution. Additional welded specimens were exposed to 8, 4, 2, and 1 weight percent sulfuric acid. The specimens spontaneously activated in all of these test solutions. Additional welded specimens were exposed to 50 and 70 weight percent H_2SO_4-6 weight percent $CuSO_4$. Intergranular corrosion was observed in boiling 50 weight percent H_2SO_4-6 weight percent $CuSO_4$, while the specimen dissolved in 70 weight percent H_2SO_4-6 weight percent $CuSO_4$ in contact with copper shot. All specimens were exposed for 1 h to boiling 50 weight percent H_2SO_4-6 weight percent $CuSO_4$ in contact with copper shot. General corrosion was observed on some of the test specimens; so, additional tests were conducted for 2 h in 50 weight percent H_2SO_4-$CuSO_4$ at 60°C (140°F).

Ferric Sulfate Test

All specimens were exposed to 50 weight percent H_2SO_4 plus ferric sulfate [$Fe_2(SO_4)_3$] according to ASTM A 262, Practice B, with the exception that the test time was reduced to 30 min. Most of the materials examined dissolved during the 30 min of exposure. No additional modifications were attempted in this test solution.

Test Results and Discussion

The results of the corrosion tests in the modified nitric acid test and in the modified cupric sulfate test are shown in Table 2 for the heat treated specimens and TIG welded specimens.

The rating of "passed" or "failed" was based on visual examination at ×30 magnification on the stereoscopic microscope before and after bending. When this method was in doubt the specimens were sectioned and examined at higher magnification on an optical microscope or a scanning electron microscope (SEM). Examples illustrating the test results in the nitric acid test are shown in Figs. 3 to 6. Intergranular corrosion in Type 409 heat treated at 1204°C (2200°F) after the nitric acid test is shown in

TABLE 2—*Corrosion of Types 409, 405, and 410 in the* (a) *modified nitric acid test and* (b) *modified cupric sulfate test.*

Alloy	Heat No.	Condition	Nitric Acid	Cupric Sulfate
409	A	982°C (1800°F)	F	P
		1093°C (2000°F)	F	P
		1204°C (2200°F)	F	P
		TIG-base	P	P
		TIG-HAZ	P	P
		TIG-weld	F	P
405	B	982°C (1800°F)	F	F
		1093°C (2000°F)	F	F
		1204°C (2200°F)	F	F*
		TIG-base	P	P
		TIG-HAZ	F	F
		TIG-weld	F	F
410	C	982°C (1800°F)	P	P
		1093°C (2000°F)	P	P
		1204°C (2200°F)	P	P
		TIG-base	P	P
		TIG-HAZ	P	P
		TIG-weld	P	P*

NOTE—F = failed; P = passed; and * = surface decarburizing.

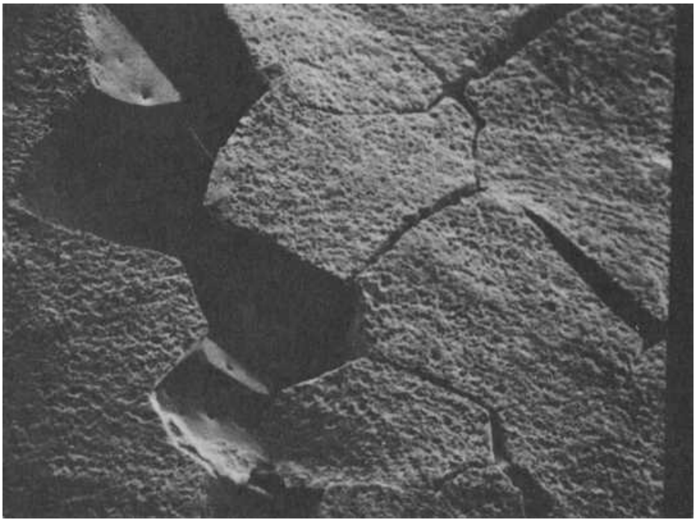


FIG. 3—*Intergranular corrosion in Type 409 heat treated at 1204°C (2200°F), nitric acid test (×100).*

the SEM photomicrograph in Fig. 3. The specimen has been bent to open up the corroded surfaces. Figures 4 and 5 show intergranular attack in a heat treated specimen and in the HAZ of TIG weld respectively of Type 405 after testing in HNO_3. Figure 6 shows Type 410 heat treated at 1204°C

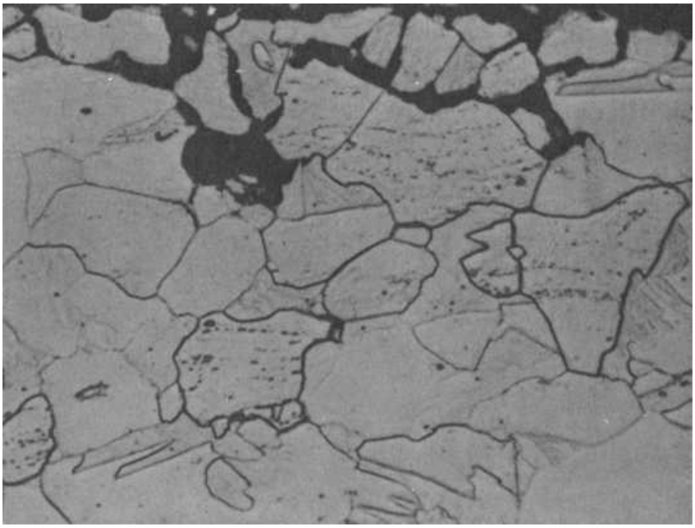


Fig. 4—*Intergranular corrosion in Type 405 heat treated at 982°C (1800°F) for 5 min, nitric acid test (×750).*

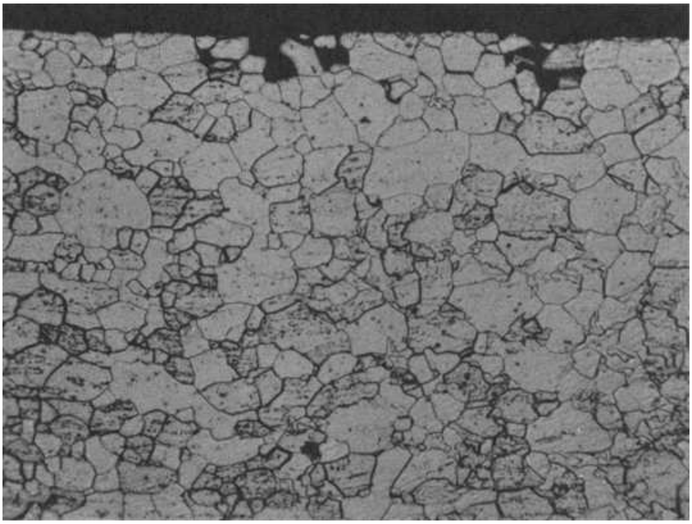


FIG. 5—*Intergranular corrosion in the HAZ of TIG welded Type 405, nitric acid test (×250).*

FIG. 6—*Intergranular corrosion in decarburized ferritic layer of Type 410 heat treated at 1204°C (2200°F). The cracks do not propagate through the martensite, nitric acid test (×250).*

(2200°F). The intergranular penetration in HNO_3, was restricted to the ferritic decarburized layer but does not proceed through martensite. For this reason this condition was rated as "passed." The extent of intergranular attack is well defined but relatively mild, indicating that there is room for optimizing the testing conditions for the 11 to 13 percent chromium steels.

The test results for Types 409 and 405 are in line with the known behavior of the higher chromium ferritic stainless steels. Type 409 being a titanium stabilized ferritic steel is similar to Types 439, 18-2Ti, and 26-1S in the sense that when heated to temperatures above approximately 982°C (1800°F) some of the titanium carbides and nitrides which are distributed uniformly are taken in solution and are precipitated at the grain boundaries during rapid cooling. The titanium carbides dissolve in HNO_3 [*11*], and all these grades fail the nitric acid test. Type 409 is, however, not susceptible to intergranular corrosion in the modified cupric sulfate test which is significant from a practical application point of view. This is also the case with the higher chromium counterparts.

Type 405 has a duplex austenitic ferritic structure at high temperature, and the closest [*12*] approach in the higher chromium steels is Type 430. Intergranular corrosion was detected by both testing methods, HNO_3 and $CuSO_4$. In Type 430 intergranular corrosion is attributed to the presence of chromium carbides which can be readily detected by optical microscopy [*5*]. In Type 405 it was, however, not possible to positively establish the presence of intergranular precipitates in the sensitized material. While intergranular corrosion could be caused by very small carbides, the possibility also exists that chromium partitioning between austenite and ferrite could produce intergranular corrosion since, as shown in Fig. 1*b*, the austenite, which is the lower chromium phase, is located primarily at the grain boundaries of the ferrite grains providing chromium depleted grain boundary zones.

It was shown by Baumel [*10*] that increasing the amount of austenite in Type 430 decreases the tendency toward intergranular corrosion since the austenite has higher carbon content and retains it in solution forming martensite. This explains the behavior of Type 410 which is completely austenitic at high temperature and transforms to martensite on cooling to room temperature, thus avoiding the formation of intergranular precipitates. For this reason Type 410 does not show intergranular corrosion in the two tests used in this work.

Anodic polarization curves were run in boiling 50 percent H_2SO_4, 50 percent H_2SO_4 plus $CuSO_4$, and 50 percent H_2SO_4 plus $Fe_2(SO_4)_3$ in an attempt to explain the behavior of Types 405, 409, and 410 stainless steels when exposed to ASTM A 262 Practice E and Practice B test solutions. The polarization behavior in these three solutions is shown for Type 409 stainless steel in Fig. 7. Type 409 stainless steel showed active-passive

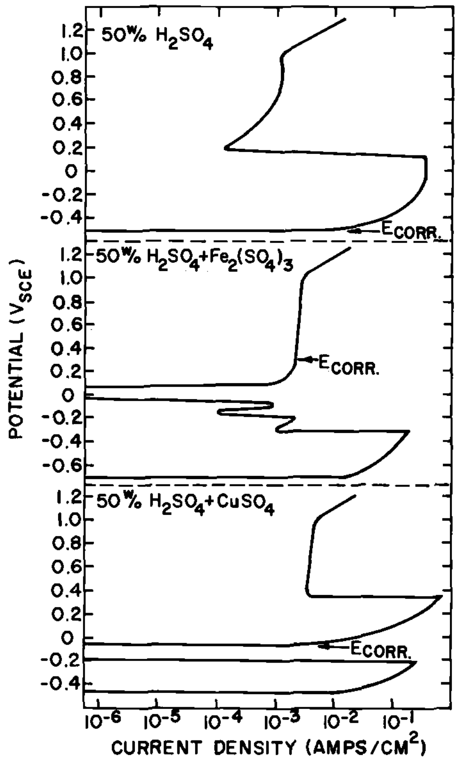


FIG. 7—*Effect of $CuSO_4$ and $Fe_2(SO_4)_3$ additions to boiling 50 weight percent H_2SO_4 on polarization behavior of Type 409 stainless steel.*

behavior in 50 percent H_2SO_4 as shown in Fig. 7 but did not spontaneously passivate in this solution. Addition of $CuSO_4$ as shown in Fig. 7 produced a cathodic loop in the anodic polarization curve over the potential range of -0.2 to -0.05 V_{SCE}. The corrosion potential with the $CuSO_4$ addition was -0.05 V_{SCE}, an active region on the polarization curve in 50 percent (H_2SO_4) with no additions. General corrosion was observed on Type 409 stainless steel in the boiling H_2SO_4-$CuSO_4$ intergranular corrosion test. The addition of $Fe_2(SO_4)_3$ to the H_2SO_4 resulted in polarization behavior as shown in Fig. 7. The initial corrosion potential was more active (-0.7 V_{SCE}) than for the other two solutions, and the steady-state corrosion potential was more noble ($+0.3$ V_{SCE}). A cathodic loop was observed in the anodic polarization curve in the potential range of -0.02 and $+0.05$ V_{SCE}. The steady-state corrosion potential was in the passive region of the anodic polarization curve in H_2SO_4 with no additions. General corrosion was not observed on Type 409 stainless steel in the H_2SO_4-$Fe_2(SO_4)_3$ test solution. General corrosion was observed on

Type 410 stainless steel in the H_2SO_4-$Fe_2(SO_4)_3$ test solution, and the steady-state corrosion potential was in the active region of the anodic polarization curve in the H_2SO_4 with no additions.

Copper deposits were observed on Types 405, 409, and 410 stainless steels after exposure to the boiling 50 percent H_2SO_4-$CuSO_4$ intergranular test solution. Anodic and cathodic polarization curves were conducted in boiling 50 percent H_2SO_4 on a pure copper specimen. The cathodic loop regions observed on the anodic polarization curves for Types 405, 409, and 410 stainless steels in the H_2SO_4-$CuSO_4$ solutions corresponded with the cathodic polarization curve for copper. The cathodic loop is proposed to be caused by the deposition of a layer of copper on the stainless steel surface. The anodic polarization curve for Type 409 stainless steel in 50 percent H_2SO_4-$CuSO_4$ in the potential range of -0.05 to $+0.36$ V_{SCE} was very similar to the anodic polarization curve for pure copper in the same potential range. The anodic polarization behavior for Type 409 stainless steel in H_2SO_4-$CuSO_4$ can be explained as follows: (1) copper deposits begin to form at the start of polarization; (2) at -0.2 V_{SCE}, the surface is covered completely with a layer of copper, and the cathodic polarization behavior of copper is observed; (3) the second active-passive region observed in the potential range of -0.05 to $+0.36$ V_{SCE} corresponds to the anodic dissolution of the deposited copper; and (4) the copper is removed essentially at $+0.36$ V_{SCE}, and the anodic behavior of Type 409 stainless steel is observed. The copper deposit that forms is apparently porous and entraps H_2SO_4 resulting in the observed general corrosion of the Type 409 stainless steel. A similar argument may be valid for the explanation of the cathodic loop observed in the H_2SO_4-$Fe_2(SO_4)_3$ solution.

Conclusions

Three commercial grades of stainless steels, Types 409, 405, and 410 were selected for the study of intergranular corrosion in 11 to 13 percent chromium steels. Type 409 is a titanium stabilized ferritic steel, Type 405 has a duplex ferritic austenitic structure at high temperatures, while Type 410 is martensitic. The results can be summarized as follows:

1. The standard ASTM A 262 corrosion tests for intergranular corrosion are too severe and cannot be applied to 11 to 13 percent chromium steels. Two modified tests were developed: (1) 65 percent HNO_3, three 48-h periods at 60°C (140°F) and (2) 50 weight percent H_2SO_4-6 weight percent $CuSO_4$ 2 h at 60°C (140°F).

2. The behavior of Type 409 is similar to that of the higher chromium titanium stabilized ferritic stainless steels; it fails the nitric acid test probably because of attack of the titanium carbides precipitated at the grain boundaries but is not susceptible to intergranular corrosion in the more relevant modified cupric sulfate test.

3. Type 405 in the sensitized condition shows intergranular corrosion in both the nitric acid and cupric sulfate tests. The most likely cause for intergranular corrosion in Type 405 is precipitation of chromium carbides at the ferrite-ferrite grain boundaries. Since no substantial amount of intergranular carbides could be found the possibility exists that chromium partitioning between ferrite and austenite, which is at the grain boundaries of the former, is the cause for intergranular corrosion.

4. Anodic polarization studies have shown qualitatively why the standard ASTM A 286 intergranular corrosion tests are too severe for Types 405, 409, and 410 stainless steels. The corrosion potential of Type 409 in 50 percent H_2SO_4 plus $CuSO_4$ was in the active region of the anodic polarization curve for Type 409 in 50 percent H_2SO_4. A cathodic loop was observed for Types 405, 409, and 410 stainless steels in 50 percent H_2SO_4 plus $CuSO_4$ and 50 percent H_2SO_4 plus $Fe_2(SO_4)_3$. The cathodic loop was explained on the basis that copper was plating on the specimen surface in the cathodic loop potential range. High corrosion rates were observed on the specimens when the copper deposits were present. It was assumed that the cathodic loop observed in 50 percent H_2SO_4 plus $FE_2(SO_4)_3$ was due to the formation of an iron deposit on the specimen surface.

Acknowledgments

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Summary

This volume contains the nine papers that resulted from the Symposium on Intergranular Corrosion of Stainless Alloys that was held in Toronto in May 1977. The papers can be divided into three categories: Introduction, Austenitic Alloys, and Ferritic Stainless Steels.

Introduction

The keynote paper of this symposium was given by M. A. Streicher. It is a wide-ranging discussion of intergranular corrosion in austenitic and ferritic stainless steels as well as some nickel-base alloys. He reviews the development of the various tests used for evaluating the resistance of stainless steels to intergranular corrosion, noting that the nitric acid and the copper sulfate-sulfuric acid tests were really designed to simulate conditions to which stainless steels were exposed during service. Once it was clear that susceptibility to intergranular corrosion is controlled by metallurgical variables, other tests were developed which could more quickly or more sensitively show the presence of those features—chromium depleted zones and intermediate phases—which can lead to intergranular corrosion.

Streicher reviews not only the A-1 tests used for quality control for stainless steels but also the G-1 tests used for nickel-base alloys and determining resistance to polythionic acid cracking. He also discusses work currently in progress to develop a standard for testing ferritic stainless steels for resistance to intergranular corrosion. He also discusses the relationship between intergranular corrosion and other forms of corrosion. Not all environments produce intergranular corrosion even of sensitized steels, but in many cases this sensitization also reduces resistance to other forms of corrosion such as pitting and stress-corrosion cracking.

After discussing when evaluation tests should be used, Streicher suggests that prudence requires that materials used in critical applications be tested for intergranular corrosion even when sensitized material has proven satisfactory. Among the reasons for such testing are the time factor and degree of sensitization. What is satisfactory for 10 years might not be for 40, and severely sensitized material can behave differently from mildly sensitized material.

In leading to the major thrust of the paper, Streicher suggests a number of steps: removal of the nitric acid test from A 262 and making it a new simulated service test, eliminating the nitric acid-hydrofluoric acid test

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from A 262, reducing the number of copper sulfate tests, including assessment criteria in all test practices, devising a heat treatment to simulate sensitization produced by welding, establishment of evaluation criteria for weldments, using the oxalic etch test as the sole basis for evaluating castings, investigation of the effects of intermetallic phases on the corrosion behavior of stainless steels and nickel-base alloys, improving the test method for determining susceptibility to polythionic acid cracking, and determining the influence of surface preparation on the corrosion behavior of nickel-base alloys. After considering each of these items, he concludes with a proposal for a major revision and consolidation of current ASTM practices for intergranular corrosion testing. The changes would occur in two stages and would require considerable intercompany cooperation.

Austenitic Alloys

Much of the work on austenitic stainless steels and alloys that was reported in this symposium was motivated by problems in nuclear systems. Taboda and Frank provide a framework for these discussions with their general paper outlining intergranular corrosion problems in nuclear systems. Since many corrosion failures in reactors involve cracking, they begin by reviewing stress-corrosion problems in early reactors. For the most part, these were experimental units, and the problems could be explained by the misapplication of austenitic steels in environments that contained excess chlorides or caustic.

The next series of failures were associated with intergranular cracking of austenitic stainless steels that had been sensitized by furnace heat treatments. In these cases, chlorides could not be definitely identified as the source of the cracking, and fluorides from welding fluxes and dissolved oxygen in the water were suspected of contributing to the problem. The solution was replacing the heavily sensitized material with low carbon alloys or weld overlays which are not subject to intergranular corrosion.

Later cracks were found in Type 304 pipes that had been sensitized by welding. The intergranular cracking appeared to be controlled by degree of sensitization, amount of dissolved oxygen, and stress level. Although this cracking was not considered serious enough to cause a public hazard, steps have been taken to avoid such conditions. These include changing to low carbon stainless steels, improving control over water chemistry, reducing stresses, and tightening leak detection and inspection practices.

Since degree of sensitization plays an important part in the intergranular stress-corrosion cracking of stainless steels, the Nuclear Regulatory Commission is sponsoring work on quantitative electrochemical tests for determining this factor. The ASTM activity in this area is handled by Subcommittee G01.08.

Taboda and Frank also reviewed the corrosion problems with Inconel

600 steam generator tubes. Although there have been some instances of intergranular corrosion of Inconel 600, no clear link has been found between this phenomenon and most failures. Water chemistry seems much more important. The National Research Council has asked ASTM to develop a test for determining the susceptibility of Inconel 600 to stress corrosion cracking in water. This is the charge of Task Group G01.06.92.

The other three papers on austenitic steels were concerned with developing quantitative measures of the degree of sensitization. Interest in this property stems, of course, from the fact that it appears to influence susceptibility to intergranular stress-corrosion cracking. It is a little surprising that none of the authors tried to use weight-loss as measured in either the ferric sulfate-sulfuric acid (A 262, Practice B) or nitric acid (A 262, Practice C) tests as a quantitative measure of sensitization.

Clarke, Cowan, and Walker used three intergranular corrosion tests to examine the relationship between degree of sensitization and resistance to intergranular stress-corrosion cracking. Resistance to this type of cracking was measured by dynamic straining in high temperature, high purity water with a very high oxygen content.

One of the intergranular corrosion tests was a modification of the oxalic acid etch test (A 262, Practice H). The modification was to measure and report the length of grain boundaries showing ditching. This method is fairly sensitive to small amounts of sensitization but cannot distinguish among specimens when all the grain boundaries have been ditched. Numerical ranking is difficult even for the lightly sensitized materials.

The authors also tried to quantify the copper-copper sulfate-16 percent sulfuric acid (A 262, Practice E) test by measuring grain boundary penetration either metallographically or by tension testing before and after exposure to the test solution. This method was not very discerning for mildly sensitized specimens, but it did show differences among the severely sensitized materials. It has the drawback of being a destructive test.

The third method used by Clarke et al was the electrochemical potentiokinetic reactivation (EPR) technique. In this test the specimen is electrochemically passivated in 0.5M H_2SO_4 + 0.01M KCNS and then reactivated by a potential sweep in the active direction. The measure of sensitivity to intergranular corrosion is the activation change Q, which is the integrated area under the reactivation curve. The theory of the method is that increased current will flow from the chromium-depleted zones during activation. This method detects low levels of sensitization and quantitatively ranks specimens in order of their susceptibility to intergranular stress corrosion cracking. However, it does reach a saturation point for severely sensitized materials. The authors feel that it is the most sensitive and quantitative of the tests they studied. They feel that it can be adapted for field tests.

Vyas and Issacs used a modification of the EPR test to investigate sensitization of welds. The basic technique is again looking at the reactivation behavior of stainless steels electrochemically passivated in an H_2SO_4-KCNS solution, but the difference is the use of two reference electrodes. One is held stationary over the unaffected base plate while the other is moved over welds and their heat-affected zones. The corrosion index is the potential difference between the scanning and fixed reference electrodes. The larger the difference, the more susceptible the material under the scanning electrode is to intergranular corrosion. The authors claim that this technique finds the location and degree of maximum sensitization. They call this test method the scanning reference electrochemical technique (SRET).

Vyas and Issacs say that their technique gives the location, a quantitative measured, and the variation in degree of sensitization of steels adjacent to a weld. The method is nondestructive and could possibly be developed into a field test. They suggest that it may be more discerning than the existing chemical methods, and their paper illustrates its use in failure analysis.

The editor has grouped Walker's paper on variations in the evaluation of the results of the copper-copper sulfate-16 percent sulfuric acid test with those concerned with the determination of the degree of sensitization because he feels that the author originally hoped that it might be possible to find some way of quantitizing the results of the Practice E bend tests.

The experimental plan was to expose specimens of one heat of sensitized Type 304 stainless steel for various times to the copper-copper sulfate-16 percent sulfuric acid solution. The specimens were then bent in the author's laboratory and sent to members of Subcommittee A01.14 for evaluation on a round robin basis. A total of 42 evaluations were the basis of the survey. Some might feel that the results of the survey are clouded by the fact that a number of the specimens were exposed for less than 24 h which is the minimum time for Practice E, but few would quarrel with the conclusion that metallographic examination is required to quantify the results of this test.

Ferritic Stainless Steels

The last four papers in the symposium deal with testing ferritic stainless steels for resistance to intergranular corrosion. There has been no ASTM recommended practice for this kind of testing because conventional ferritic stainless steels are not often used where corrosion resistance is critical. However, the recent development of ferritic stainless steels with greatly improved properties has led to their application in a variety of chemical environments. A task group of Subcommittee A01.14 is now working on a recommended practice for evaluating the resistance of ferritic stainless steels in intergranular corrosion, and therefore these papers are particularly timely.

Dundas and Bond investigated the amounts of titanium and niobium required to stabilize 18Cr-2Mo and 26Cr-1Mo steels against intergranular corrosion. For evaluation tests they used the oxalic acid etch test (A 262, Practice A), the ferric sulfate-sulfuric acid test (A 262, Practice B), the nitric acid-hydrofluoric acid test (A 262, Practice D), the copper-copper-sulfate-16 percent sulfuric acid test (A 262, Practice E), and a copper-copper sulfate-50 percent sulfuric acid test. They compared the results of the evaluation tests with general corrosion in boiling formic acid, pitting in ferric chloride, and stress-corrosion cracking in boiling seawater. Welding and heat treatment were used for sensitization.

For 18Cr-2Mo steels the oxalic acid etch and the two copper sulfate tests gave the same results. The criterion used for the copper-copper sulfate-50 percent sulfuric acid test was the absence of grain dropping after testing. These tests were also suitable for the 26Cr-1Mo steels. The nitric acid-hydrofluoric acid test caused intergranular attack in understabilized 26Cr-1Mo steels; metallographic examination was required to reveal it.

The ferric sulfate-sulfuric acid test gave variable results on 26Cr-1Mo alloys (18Cr-2Mo was not tested in this solution). Results on niobium-stabilized alloys agreed with those from the other tests, but the titanium-stabilized steels were subject to intergranular attack in the ferric sulfate solution even when they passed the other tests. It may be that it attacks titanium compounds directly or reveals an "invisible" phase that is troublesome only in highly oxidizing environments.

The results of the boiling acid, pitting, and stress-corrosion tests indicate that the corrosion resistance of ferritic stainless steels will be impaired if they are subject to intergranular corrosion in the evaluation tests. The results on specimens that were slowly cooled from 1205°C were similar to those on welded specimens; therefore, this treatment may be a suitable laboratory sensitizing treatment. For 18Cr-2Mo and 26Cr-1Mo steels containing 0.02 to 0.05 percent (C + N) Dundas and Bond found that a minimum amount of stabilizer required to avoid susceptibility to intergranular corrosion is given by: $Ti + Nb = 4 (C + N) + 0.2$.

Nichol and Davis investigated the effects of alloy chemistry and thermal history on the susceptibility of 29Cr-4Mo and 26Cr-1Mo-Ti ferritic stainless steels. The 29Cr-4Mo alloy relies on a low interstitial content for resistance to sensitization; whereas, the 26Cr-1Mo-Ti is stabilized. They used the same immersion tests as Dundas and Bond. Their results ranked the tests in order of increasing severity; copper-copper sulfate-16 percent sulfuric acid, nitric acid-hydrofluoric acid, copper-copper sulfate-50 percent sulfuric acid, ferric sulfate-50 percent sulfuric acid. They, too, found that the ferric sulfate test was not satisfactory for 26Cr-1Mo-Ti. Although they measured weight loss in all the tests, they found it an unreliable criterion of intergranular attack in these high chromium alloys. They recommend bending the material and examining it optically for evidence of grain dropping. They used both heat treatment and welding to produce sensitization.

Sweet studied the susceptibility of welded 26Cr-1Mo-Ti ferritic stainless steels in a number of evaluation tests, simulated plant environments, and the wick test for chloride stress corrosion cracking. He concluded that welding understabilized 26Cr-1Mo-Ti reduces its corrosion resistance in a variety of media including those that would cause stress-corrosion cracking in austenitic stainless steels. Therefore, he recommends the use of evaluation tests for the acceptance of this alloy.

He finds that the oxalic acid etch test is useful in determining whether or not material is sensitized. Of the immersion tests, he prefers the copper-copper sulfate-50 percent acid with microscopic examination for grain dropping. As did Dundas and Bond, and Nichol and Davis, he found that the ferric sulfate-sulfuric acid test produced intergranular corrosion in material that is immune to this type of attack in the other solutions. He also attributes this to direct attack of titanium-rich phases, but he cautions this fact must be taken into account when considering titanium-stabilized alloys for service in highly oxidizing environments.

Sweet feels that a Ti/C + N ratio of at least 10 is required to ensure that 26Cr-1Mo-Ti alloys are stabilized. The specification for XM-33 currently has a minimum ratio of 7.

It is encouraging that the three papers on the intergranular corrosion behavior of the new ferritic stainless steels are in fairly good agreement. The fact that the copper-copper sulfate-50 percent sulfuric acid test is acceptable to all may point the way for a simpler recommended practice as Streicher suggests. It is also interesting that three different laboratories were able to reach substantially the same conclusions using welded specimens. Perhaps the use of a bend test or the grain dropping criterion is the answer to the nagging question of how to evaluate welds.

In the final paper of the symposium, Lula and Davis examined the intergranular corrosion behavior of some 12Cr stainless steels. Traditionally these alloys have not been used in anything but the mildest service, but there is some tendency now to use them in somewhat more demanding service. Three steels were investigated: Type 409 a titanium-stabilized ferritic stainless steel, Type 405 a ferritic steel that can transform partially to austenite at high temperatures, and Type 410 a martensitic steel.

When tested in the copper-copper-sulfate-16 percent sulfuric acid, the nitric acid, or the ferric sulfate-sulfuric acid tests as described in A 262, none of the steels survived. Therefore, the authors modified the nitric acid test by lowering the temperature to 60°C and reducing the exposure time to three 48-h periods. The copper sulfate test was modified by raising the acid concentration to 50 percent, dropping the temperature to 60°C, and cutting the time to 2 h. Both tests did produce intergranular corrosion.

As one might expect because of its titanium content welded Type 409 suffered intergranular corrosion in nitric acid. It passed the copper sulfate test, however. Type 405 was subject to intergranular corrosion in both tests, and Type 410 in neither. These results are consistent with the microstructural changes that occur during the welding of these alloys.

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Index

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