Use of Duplex Stainless Steels in the Oil Refining Industry

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Introduction

Duplex stainless steels (DSSs) are finding increasing use in the refining industry, primarily because they often offer an economical combination of strength and corrosion resistance. These stainless steels (SSs) typically have an annealed structure that is generally half ferrite and half austenite, although the ratios can vary from approximately 35/65 to 55/45. Most refinery applications where DSSs are used are corrosive, and DSSs or other higher alloys are required for adequate corrosion resistance. However, some plants are also starting to consider DSS as a “baseline” material [1]. These plants are using DSS in applications where carbon steel may be acceptable, but DSSs have been shown to be more economical, considering their higher strength and better long-term reliability.

DSSs are often used in lieu of austenitic SS in services where the common austenitics would have problems with chloride pitting or chloride stress corrosion cracking (CSCC). Higher alloyed DSSs like super duplex and hyper duplex are an economic alternative to higher alloys with similar corrosion resistance. Figure 1 (in Section 1) shows a comparison of DSSs with various austenitic SSs, showing the difference in strength and chloride corrosion resistance (expressed as pitting resistance equivalent number [PREN], which is defined in 5.1) [2]. This chart shows the excellent combinations of higher strength and corrosion resistance available with DSSs. It also indicates that there are “subfamilies” of specific grades within both the DSSs and austenitic families. This is also illustrated in Table 1 (in Section 1).

DSSs have existed since the 1930s. However, the first generation steels, such as Type 329 (UNS S32900) had unacceptable corrosion resistance and toughness at weldments [3], [4], [5]. Hence, the initial applications were almost exclusively for heat exchanger tubing, particularly in corrosive cooling water services, and shafting or forgings. In the 1980s, second generation DSSs became commercially available which helped overcome the problems at the welds. These new grades had nitrogen additions and better austenite/ferrite balances, which along with improved welding practices designed for the DSSs, led to the welds’ mechanical (strength and toughness) and corrosion properties being comparable to the annealed base metal. The DSSs most commonly used today in refineries include those with 22 %, 25 % and 27 % Cr. The 25 % Cr (super duplex grades) and 27 % Cr (hyper duplex grade) usually also contain more molybdenum and nitrogen, and so have higher PREN values than the 22 % Cr duplex steels.

Table 1 lists the compositions and UNS numbers of various common DSSs, including some first generation DSSs for comparison. Note that UNS S32205 is a “newer version” of UNS S31803 and while it also meets the S31803 chemistry, it is produced with higher minimum nitrogen, chromium, and molybdenum contents. In many cases, material is dual-certified as S31803/S32205. ASME and ASTM standards for duplex SS grades are given in Table 2 (in Section 1), while Table 3 (in Section 1) provides the mechanical properties. Type 316L and other austenitic SS are included in these tables for comparison.

This report has four primary objectives, which are to describe:

a) potential environment-related failure mechanisms and preventative measures to avoid them;

b) typical material specification requirements used by refiners;

c) typical fabrication specification requirements used by refiners;

d) examples of applications of DSSs within refineries.

Use of Duplex Stainless Steels in the Oil Refining Industry

1 Scope

This report covers many of the “lean”, “standard”, “super”, and “hyper” grades of duplex stainless steels (DSSs) most commonly used within refineries. The definitions of these terms have not been firmly established by the industry, and vary between literature references and materials suppliers. Table 1 shows how the various grades are being classified into “families” for the purposes of this report. The UNS numbers of the standard grades being used for corrosive refining services include:

— Lean DSSs: S32101, S32202, S32304, S32003, S82011, and S82441;

— Standard DSSs: S31803 and S32205;

— Super DSSs: S32520, S32550, S32750, S32760, and S32906;

— Hyper DSS: S32707.

The grades which are labeled as “lean” (including grades sometimes called “semi-lean”) have either lower Cr, Ni, or Mo than the standard grades, and are used in some process services that are less aggressive (primarily in corrosive environments to replace 304L SS). These alloys have also been used for storage tanks and structural applications, primarily for their higher strength as compared to carbon steel (CS). It is observed that new DSS alloys are being introduced and are likely to continue to be introduced. These new grades can be reasonably placed in the context of this discussion based on their composition.

The product forms within the scope are tubing, plate, sheet, forgings, pipe, and fittings for piping, vessel, exchanger, and tank applications. The use of DSSs for tanks is also addressed by API 650, Annex X. The Third Edition of this report (API 938-C) has added sections covering castings and hot isostatically-pressed (HIP) components for pumps, valves, and other applications. The limited use of DSSs as a cladding is also briefly covered within this document.

The majority of refinery services where DSSs are currently being used or being considered in the refining industry contain:

a) a wet, sour (H_2S) environment, which may also contain hydrogen, ammonia, carbon dioxide, chlorides, and/or hydrocarbons, which typically has a pH greater than 7;

b) water containing chlorides, with or without hydrocarbons—this includes many fresh water cooling water systems, and some salt water systems with higher alloy grades;

c) hydrocarbons with naphthenic acids at greater than 200 °C (400 °F), but below the maximum allowable temperatures in the ASME Code for DSSs (260 °C to 343 °C [500 °F to 650 °F], depending on the grade);

d) amines, such as MEA, MDEA, DEA, etc.; or

e) other environments, such as those containing caustic conditions.

The specific plant locations containing these services are described in a later section and the report scope will be limited to the first four environments. Although DSSs have good resistance to caustic environments, this service is not unique to or widespread in refining, and hence is not covered in detail in this report.

Table 1—Chemical Compositions of Commonly Used DSSs and Other Alloys

Mass % [a, e]													
UNS Number	Type [b]	Cr	Mo	Ni	N	Cu	C	Mn	P	S	Si	Min PREN (bulk) [d,f]	Other
First Generation DSSs													
S32900	Type 329	23.0 to 28.0	1.0 to 2.0	2.5 to 5.0	—	—	0.080	1.00	0.040	0.030	0.75	26.3 [f]	—
S31500	"3RE60"	18.0 to 19.0	2.5 to 3.0	4.25 to 5.25	0.05 to 0.10	—	0.030	1.20 to 2.00	0.030	0.030	1.40 to 2.00	27.1 [f]	
Lean DSSs													
S32304	2304 [c]	21.5 to 24.5	0.05 to 0.60	3.0 to 5.5	0.05 to 0.20	0.05 to 0.60	0.030	2.50	0.040	0.030	1.00	22.5 [f]	—
S32101	2101	21.0 to 22.0	0.10 to 0.80	1.35 to 1.70	0.20 to 0.25	0.10 to 0.80	0.040	4.0 to 6.0	0.040	0.030	1.00	24.5 [f]	—
S32202	2202	21.5 to 24.0	0.45	1.00 to 2.80	0.18 to 0.26	—	0.030	2.00	0.040	0.010	1.00	24.4 [f]	
S32003	2003	19.5 to 22.5	1.50 to 2.00	3.0 to 4.0	0.14 to 0.20	—	0.030	2.00	0.030	0.020	1.00	26.7 [f]	—
S82011	2102	20.5 to 23.5	0.10 to 1.00	1.0 to 2.0	0.15 to 0.27	0.50	0.030	2.00 to 3.00	0.040	0.020	1.00	23.1 [f]	
S82441	2404	23.0 to 25.0	1.00 to 2.00	3.0 to 4.5	0.20 to 0.30	0.10 to 0.80	0.030	2.5 to 4.0	0.035	0.005	0.70	29.5 [f]	
Standard DSSs													
S31803	—	21.0 to 23.0	2.5 to 3.5	4.5 to 6.5	0.08 to 0.20	—	0.030	2.00	0.030	0.020	1.00	30.5 [f]	—
S32205	2205 [c]	22.0 to 23.0	3.0 to 3.5	4.5 to 6.5	0.14 to 0.20	—	0.030	2.00	0.030	0.020	1.00	34.1 [f]	—
Super DSSs													
S32520	—	24.0 to 26.0	3.0 to 5.0	5.5 to 8.0	0.20 to 0.35	0.50 to 3.00	0.030	1.50	0.035	0.020	0.80	37.1 [f]	
S32550	255 [c]	24.0 to 27.0	2.9 to 3.9	4.5 to 6.5	0.10 to 0.25	1.50 to 2.50	0.040	1.50	0.040	0.030	1.00	35.2 [f]	—
S32750	2507 [c]	24.0 to 26.0	3.0 to 5.0	6.0 to 8.0	0.24 to 0.32	0.50	0.030	1.20	0.035	0.020	0.80	37.7 [f]	—
S32760	"Z100"	24.0 to 26.0	3.0 to 4.0	6.0 to 8.0	0.20 to 0.30	0.50 to 1.00	0.030	1.00	0.030	0.010	1.00	40.0 [d]	W: 0.5 to 1.0
S32906		28.0 to 30.0	1.50 to 2.60	5.8 to 7.5	0.30 to 0.40	0.80	0.030	0.80 to 1.50	0.030	0.030	0.80	37.8 [f]	

Table 1—Chemical Compositions of Commonly Used DSSs and Other Alloys (Continued)

		Mass % [a, e]											
UNS Number	**Type** [b]	**Cr**	**Mo**	**Ni**	**N**	**Cu**	**C**	**Mn**	**P**	**S**	**Si**	**Min PREN (bulk)** [d,f]	**Other**
Hyper DSSs													
S32707	2707 [c]	26.0 to 29.0	4.0 to 5.0	5.5 to 9.5	0.30 to 0.50	1.00	0.030	1.50	0.035	0.010	0.50	44.0	Co: 0.5 to 2.0
Austenitic SS													
S31603	Type 316L	16.0 to 18.0	2.0 to 3.0	10.0 to 14.0	0.10	—	0.030	2.00	0.045	0.030	0.75	22.6	—
S31703	Type 317L	18.0 to 20.0	3.0 to 4.0	11.0 to 15.0	0.10	—	0.030	2.00	0.045	0.030	0.75	27.9	—
N08020	"Alloy 20"	19.0 to 21.0	2.0 to 3.0	32.0 to 38.0	—	3.00 to 4.00	0.070	2.00	0.045	0.035	1.00	25.6	Cb + Ta: 8×C – 1.00
N08904	904L	19.0 to 23.0	4.0 to 5.0	23.0 to 28.0	0.10	1.00 to 2.00	0.020	2.00	0.040	0.030	1.00	32.2	
6 % Mo Super Austenitic SS													
N08367	—	20.0 to 22.0	6.0 to 7.0	23.5 to 25.5	0.18 to 0.25	0.75	0.030	2.00	0.040	0.030	1.00	42.7	—
S31254	—	19.5 to 20.5	6.0 to 6.5	17.5 to 18.5	0.18 to 0.22	0.50 to 1.00	0.020	1.00	0.030	0.010	0.80	42.2	—
N08926	—	19.0 to 21.0	6.0 to 7.0	24.0 to 26.0	0.15 to 0.25	0.50 to 1.50	0.020	2.00	0.030	0.010	0.50	41.2	—

[a] Single values indicate maximum content unless otherwise specified. The number of significant figures reflects the ASTM recommended practices as shown in ASTM A959, ASTM A240, and ASTM A789, but these rules have not yet been universally adopted for all product forms and all specifications systems.

[b] Unless otherwise indicated, a grade designation originally assigned by the American Iron and Steel Institute (AISI). Names shown in quotation marks are not listed in ASTM specifications.

[c] As listed by ASTM, a widely-used common name (not a trademark and not associated with any one producer).

[d] Minimum PREN (see equations in 5.1) is calculated based on the minimum chemistry requirements based on the overall alloy chemistry—see footnote f. Note that UNS S32760, which has a minimum PREN of 40 required by ASTM/ASME material specifications.

[e] The chemistry may vary slightly between product forms and the specifications often change with time. Hence, for the latest chemistry requirements, the product specifications should be reviewed.

[f] With duplex SS grades with a PREN less than about 40, there can be a difference between the PREN based on the overall chemistry versus the PRENs of the austenite grains and the ferrite grains. In standard duplex SS grades, the austenite can have a lower PREN, and in the lean duplex SS grades, the ferrite can have a lower PREN, compared to the PREN based on overall chemistry. In some severe services, this has led to selective attack of the phase with the lower PREN.

Table 2—ASME and ASTM Specifications for DSSs

Product Form	ASME or ASTM Specifications
Plate, Sheet	SA-240
Bar Products	SA-479, A276
Pipe	SA-790, A928
Tubing	SA-789
Fittings	SA-815
Forgings	SA-182
Castings	SA-351, A890, A995
HIP Products	ASTM A988
Bolting	ASTM A1082
Testing	ASTM A923, ASTM G48, ASTM A1084

Table 3—Mechanical Properties of Various Duplex and 316L SSs

UNS Number	Type	Tensile Strength, min		Yield Strength, min		Elongation min %	Hardness, max	
		Mpa	ksi	Mpa	ksi		Brinell	Rockwell C
S32304	2304	600	87	400	58	25.0	290	—
S32101	2101	650	95	450	65	30.0	290	—
S32202	2202	650	94	450	65	30.0	290	—
S32003	2003	620	90	450	65	25.0	293	31
S82011 (>5 mm)	2102	655	95	450	65	30	293	31
S82441 (≥10 mm)	2404	680	99	480	70	25	290	—
S31803	—	620	90	450	65	25.0	293	31
S32205	2205	655	95	450	65	25.0	293	31
S32550	255	760	110	550	80	15.0	302	32
S32750	2507	795	116	550	80	15.0	310	32
S32760	Z100	750	108	550	80	25.0	270	—
S32906 (≥4 mm)	—	750	109	550	80	25.0	310	32
S32707 [a]	2707	920	133	700	101	25	318	34
S31603	316L	485	70	170	25	40.0	217	95 R_b [c]
N08825 [b]	825	586	85	241	35	30.0	—	—

NOTE The values shown are for ASME SA-240 plate grades (except as noted below), and may vary slightly between product forms. Also, specifications often change with time. Hence, for the latest requirements, the product specifications should be reviewed.

[a] The values shown are for ASTM A789 tubing under 4 mm wall, since this material is not yet available in ASME SA-240 as plate form.

[b] N08825 is a nickel-based alloy shown for comparison purposes and its mechanical properties are based on ASME SB-424.

[c] This limit is below the Rockwell C scale and hence is reported as Rockwell B.

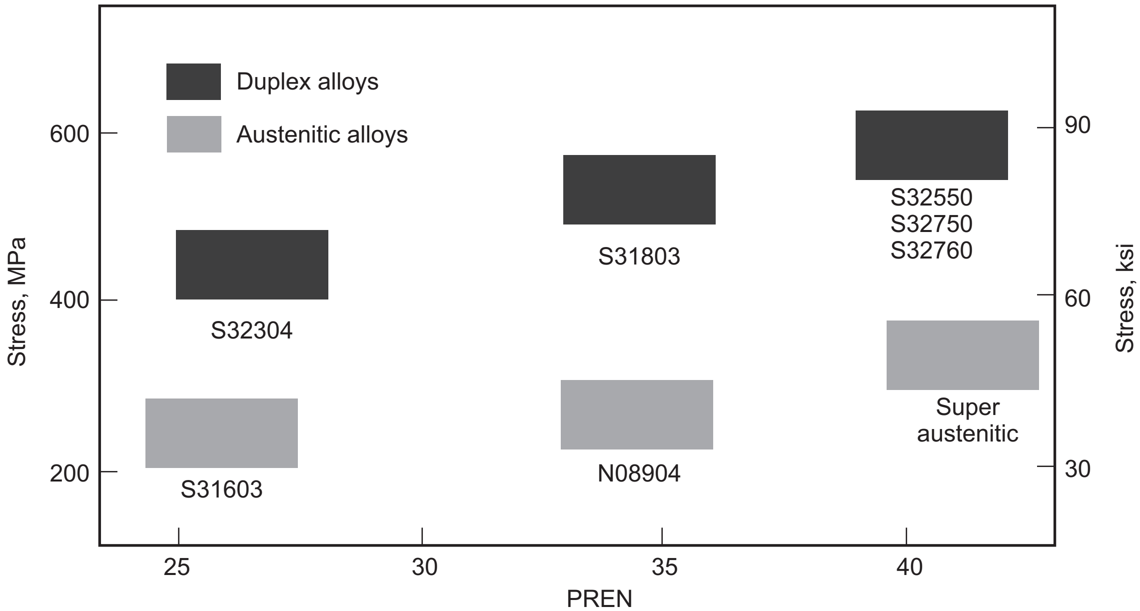

Figure 1—Comparison of the Proof Stress and Pitting Resistance (based on PREN of the bulk chemistry) of Duplex and Austenitic SS [2]

2 Normative References

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

API Recommended Practice 578, *Material Verification Program for New and Existing Alloy Piping Systems*

API Recommended Practice 582, *Welding Guidelines for the Chemical, Oil, and Gas Industries*

API Standard 650, *Welded Tanks for Oil Storage*

API Recommended Practice 932-B, *Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems*

ASME *Boiler and Pressure Vessel Code (BPVC)* [1], *Section VIII : Pressure Vessels; Division 1, Division 2*

ASME *BPVC*, Section IX: “Welding and Brazing Qualifications”

ASME B31.3, *Process Piping*

ASME SA-182,*Specification for Forged or Rolled Alloy-Steel Pipe Flanges, Forged Fittings, and Valves and Parts for High-Temperature Service*

ASME SA-240, *Specification for Heat-Resisting Chromium and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Pressure Vessels*

ASME SA-351, *Specification for Castings, Austenitic, Austenitic-Ferritic (Duplex), for Pressure-Containing Parts*

ASME SA-479, *Specification for Stainless Steel Bars and Shapes for Use in Boilers and Other Pressure Vessels*

[1] ASME International, 2 Park Avenue, New York, New York 10016-5990, www.asme.org.

ASME SA-789, *Specification for Seamless and Welded Ferritic/Austenitic Stainless Steel Tubing for General Service*

ASME SA-790, *Specification for Seamless and Welded Ferritic/Austenitic Stainless Steel Pipe*

ASME SA-815, *Specification for Wrought Ferritic, Ferritic/Austenitic, and Martensitic Stainless Steel Piping Fittings*

ASTM A276 [2], *Standard Specification for Stainless Steel Bars and Shapes*

ASTM A890, *Standard Specification for Castings, Iron-Chromium-Nickel-Molybdenum Corrosion-Resistant, Duplex (Austenitic/Ferritic) for General Application*

ASTM A923, *Standard Test Methods for Detecting Detrimental Intermetallic Phase in Duplex Austenitic/Ferritic Stainless Steels*

ASTM A928, *Standard Specification for Ferritic/Austenitic (Duplex) Stainless Steel Pipe Electric Fusion Welded with Addition of Filler Metal*

ASTM A988, *Standard Specification for Hot Isostatically-Pressed Stainless Steel Flanges, Fittings, Valves and Parts for High-Temperature Service*

ASTM A995, *Standard Specification for Castings, Austenitic-Ferritic (Duplex) Stainless Steel, for Pressure-Containing Parts*

ASTM A1082, *Standard Specification for High Strength Precipitation Hardening and Duplex Stainless Steel Bolting for Special Purpose Applications*

ASTM A1084*, Standard Test Method for Detecting Detrimental Phases in Lean Duplex Austenitic/Ferritic Stainless Steels*

ASTM E140, *Standard Hardness Conversion Tables for Metals Relationship Among Brinell Hardness, Vickers Hardness, Rockwell Hardness, Superficial Hardness, Knoop Hardness, Scleroscope Hardness, and Leeb Hardness*

ASTM E562, *Standard Test Method for Determining Volume Fraction by Systematic Manual Point Count*

ASTM G48, *Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution*

AWS A4.2 [3], *Standard Procedures for Calibrating Magnetic Instruments to Measure the Delta Ferrite Content of Austenitic and Duplex Ferritic-Austenitic Stainless Steel Weld Metal*

NACE MR0103 [4], *Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments*

NACE MR0175/ISO 15156, *Petroleum and Natural Gas Industries—Materials for Use in H_2S-Containing Environments in Oil and Gas Production*

NACE SP0198, *Control of Corrosion Under Thermal Insulation and Fireproofing Materials—A Systems Approach*

NACE TM0177, *Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking and Stress Corrosion Cracking in H_2S Environments*

NIST 8481 [5], *Secondary Ferrite Number Standard—High Range*

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2 ASTM International, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428, www.astm.org.
3 American Welding Society, 8669 NW 36 Street, #130, Miami, Florida 33166-6672, www.aws.org.
4 NACE International (formerly the National Association of Corrosion Engineers), 1440 South Creek Drive, Houston, Texas 77084-4906, www.nace.org.
5 National Institute of Standards and Technology, 100 Bureau Drive, Stop 3460, Gaithersburg, Maryland 20899, www.nist.gov.

3 Terms, Definitions, and Acronyms

3.1 Terms and Definitions

For the purposes of this document, the following definitions apply.

3.1.1
duplex stainless steel
DSS
Stainless steels that are approximately 50 % austenitic and 50 % ferritic phases.

3.1.2
heat-affected zone
HAZ
The zone of base metal typically 0.5 mm to 4 mm (0.02 in. to 0.16 in.) wide adjacent to weld fusion lines, which may have been microstructurally affected by the heat of welding. This zone typically has high residual welding stresses, unless PWHT is done, and the stresses can extend beyond the HAZ. For modern DSSs, the transformed zone is typically a maximum of 0.5 mm (0.02 in.) wide when proper weld procedures are used. Heat-affected zones can be prone to certain stress corrosion cracking or corrosion mechanisms, depending on the material and service conditions.

3.1.3
naphthenic acid
Organic, carboxylic acids which are present in certain crudes and distilled streams from a crude distillation unit, and can cause corrosion at high temperatures.

3.1.4
weld
The weld deposit composed of either melted filler metal diluted with some melted base metal, or solely melted base metal. Fusion welds made with no added filler metal are called autogenous welds.

3.1.5
weldment
The weld deposit, base metal heat-affected zones and the adjacent base metal zones subject to residual stresses from welding.

3.2 Acronyms

AOD	argon oxygen decarburized
CCT	critical crevice corrosion temperature
CPT	critical pitting temperature
CS	carbon steel
CSCC	chloride stress corrosion cracking
CW	cooling water
DSS	duplex stainless steel
EDS	energy dispersive spectroscopy
ESR	electro-slag re-melt
ESW	electro-slag welding
FCAW	flux-cored arc welding

FCC	fluidized catalytic cracking
FCCU	fluidized catalytic cracking unit
FN	ferrite number
GMAW	gas metal-arc welding
GTAW	gas tungsten-arc welding
HBW	Brinell hardness number (using specific test equipment)
HIP	hot isostatically-pressed
HRC	Rockwell C hardness number
HRSG	heat recovery steam generator
HSC	hydrogen stress cracking
HV	Vickers hardness number
JIP	joint industry sponsored research project
LDSS	lean duplex stainless steel
MIC	microbiologically influenced corrosion
MDMT	minimum design metal temperature
MT	magnetic particle testing
NDE	nondestructive examination
PAW	plasma-arc welding
PQR	procedure qualification record
PREN	pitting resistance equivalent number
PT	liquid penetrant testing
PWHT	post-weld heat treatment
REAC	reactor effluent air cooler
RT	radiographic testing
SAW	submerged-arc welding
SCC	stress corrosion cracking
SDSS	super duplex stainless steel
SEM	scanning electron microscope
SMAW	shielded metal-arc welding
SS	stainless steel
SSC	sulfide stress cracking
SWS	sour water stripper
TSA	thermal sprayed aluminum
TWI	The Welding Institute
UT	ultrasonic testing
VAR	vacuum arc re-melt
VOD	vacuum oxygen decarburized
WPS	welding procedure specification

4 Metallurgy of DSSs

4.1 Background

To achieve the proper specification of the materials combined with proper fabrication and welding practices in order to obtain the expected toughness and corrosion resistance, an understanding of the metallurgical structure of DSSs and the effects of various treatments on that structure is needed. Therefore, the metallurgy of DSSs is one of the first topics covered in this report. The subsequent discussion covers the resistance of DSSs to specific degradation mechanisms and generally assumes properly produced and fabricated base materials and welds unless otherwise indicated.

Both the early and current grades of DSSs have good localized corrosion resistance in the annealed condition because of their high chromium and molybdenum contents. When the first generation duplex grades were welded, however, they lost the optimal phase balance. Excessive ferrite and precipitated sigma phase in the weld and weld HAZ adversely affected both corrosion resistance and toughness. This problem was overcome in the 1980s by the addition of nitrogen, which achieved a better balance between austenite and ferrite. Nitrogen was initially added as an inexpensive austenite former. However, this addition quickly showed other benefits, including retarded sigma phase precipitation, improved toughness, tensile and yield strength, and improved pitting and crevice corrosion resistance. Close attention to the weld procedure is still necessary to obtain the optimum results.

4.2 Solidification

DSSs solidify as a fully ferritic structure and then with further cooling, some of the ferrite transforms to austenite within the ferritic structure. Nitrogen raises the temperature at which the austenite formation begins. This allows the equilibrium level of austenite and the desired phase balance to be achieved, even at relatively rapid cooling rates. This favorable effect occurs during solidification, as in casting and welding, and in annealing and other high temperature exposures, such as the HAZ during welding. It reduces the risk of excess ferrite in the HAZ, as discussed in 4.3.

In some grades of DSS, the partitioning of the some alloying elements such as Cr, Ni, N, or Mo, can lead to differences in the corrosion resistance between the phases to certain environments. For example, Selective Austenite Attack has occurred on S32205 DSS in certain types of Flue Gas Desulfurization (FGD) units, while other services have had Selective Ferrite Attack. This is discussed further in 5.1 and 5.5. Although partitioning depends on both the chemistry and the thermal history, Table 4 shows partitioning test results of various grades [40].

Table 4—Partitioning of Elements of Various DSS Grades (% in ferrite/% in austenite)

Grade	Cr	Ni	Mo	N	Si	Cu	Mn
S32205	1.2	0.58	1.72	0.2	—	—	—
S32750	1.13	0.70	1.3	0.125	—	—	—
S32750	1.12	0.60	1.58	—	1.19	—	0.95
S32760	1.16	0.65	1.57	—	1.10	0.73	0.94

4.3 Problems to be Avoided During Welding

There are two primary problems to be avoided when welding DSSs, namely:

1) excessive ferrite in the HAZ or weld deposit;

2) formation of harmful intermetallic phases (such as sigma phase or chi phase, which are complex compounds of iron, chromium, and molybdenum) in the HAZ and weld deposit.

High ferrite contents can result from extremely low heat input welding or from extremely rapid quenching. Rapid quenching is damaging to DSSs if it causes the steel to remain mostly ferritic as it cools from the high temperature exposure. The effect of higher nitrogen content is to promote rapid formation of austenite, making the DSSs less sensitive to this problem. In virtually every case, the quenching rates fast enough to cause excessive ferrite are due to low heat input welds performed on heavy sections, with the conduction in the workpiece itself providing the rapid quench. Resistance welds, welds of sheet liners to plates, or tube-to-tubesheet welds are examples of situations susceptible to extremely rapid cooling. Another example has been small wash passes on large welds that have cooled to ambient temperature.

High ferrite content from welding is less pronounced with super and hyper duplex grades since their higher nickel and nitrogen contents help to promote austenite formation during rapid cooling processes.

This risk can be overcome by welding practices, such as preheat or controlled heat input, which counteract the tendency to excessively fast cooling of the weld and HAZ. Preheat should be performed with great care. Excessive preheat and interpass temperatures will result in too slow cool down of the material with risk of formation of intermetallic phases. Suggested limits on the ferrite content in weld and HAZ (appropriate for most refinery applications) are given in API 582. Mockups are typically required for tube-to-tubesheet welding procedure qualifications to show that the proper phase balance is achieved.

The formation of harmful intermetallic phases results from excessively high heat inputs or more accurately, excessive cumulative time at high temperatures (700 °C to 955 °C [1300 °F to 1750 °F]), as shown in Figure 2. They are extremely detrimental to impact toughness and corrosion resistance. [4], [5] The rate of this diffusion-controlled process is most rapid at 815 °C to 870 °C (1500 °F to 1600 °F) and phase formation is cumulative with each exposure. The exposure times shown below for having unacceptable amounts of intermetallic phase formation are given to show a relative comparison between the alloy families and precise values would vary by composition and other variables:

— for a 22 % Cr DSSs with nitrogen >0.14 %, about short times (significantly less than one hour) of exposure at 870 °C (1600 °F) will result in a significant loss of corrosion resistance and toughness;

— super and hyper DSSs will show similar degradation after even shorter times (minutes) at 850 °C (1560 °F);

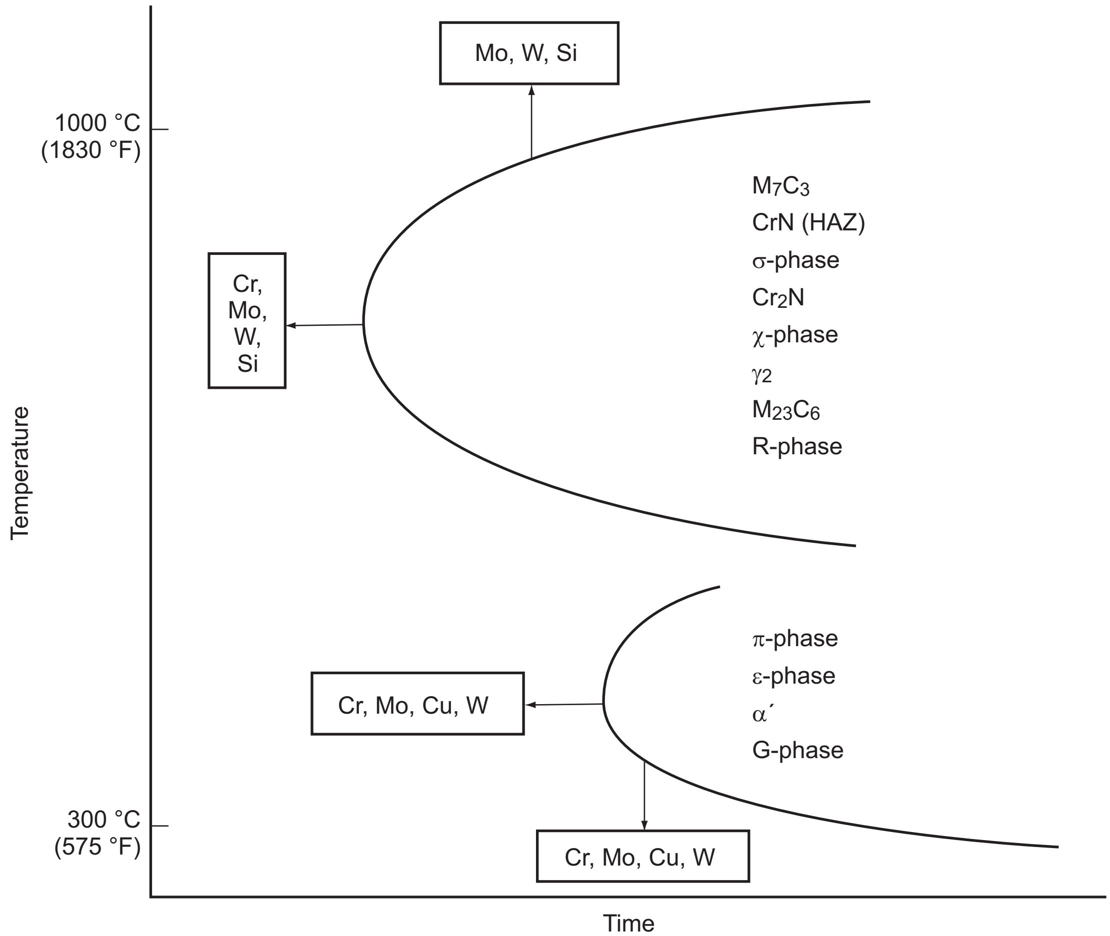
— lean DSSs, such as S32304, are much more tolerant of time in this temperature range and can be exposed for hours (typically over 10 hours) before being affected.

The cumulative exposures include the cooling time after the final annealing process and all welding (including future repairs), hot forming, and thermal treatments (other than annealing).

Because the cooling provided by the work piece itself is the most effective method of reducing the time that the HAZ and weld deposit are in the temperature range for formation of intermetallic phases, a low interpass temperature during welding is desirable for minimizing the formation of intermetallic phases. The limit can vary based on the welding procedure, metal thickness, and material grade, and typically is between 100 °C to 200 °C (210 °F to 390 °F). Once intermetallic compounds form, they can only be removed by a full anneal with sufficient time at temperature to dissolve the intermetallic compounds, followed by rapid cooling to prevent reformation. Such a treatment may not be possible on a large fabrication, such as a vessel or tank. In that case, it would be necessary to cut out the affected region and make a qualified repair.

4.4 Low and High Temperature Properties

DSSs with the proper structure can have adequate toughness for arctic ambient temperatures, but not for cryogenic applications. Minimum allowable temperatures are –51 °C (–60 °F) in the ASME B31.3 Code and –29 °C (–20 °F) for some cases in ASME Section VIII. These limits have qualifiers involving thickness, etc., and lower temperatures can be used by impact testing the material [6]. Hence, actual limits are determined by reviewing the applicable Code.



NOTE Similar curves are also shown in Figure 11, which shows the different curves for different grades of DSS.

Figure 2—Possible Precipitations in DSSs [2]

The toughness of weld deposits varies by the welding process due to the differences in the amount of oxygen in the weld typical for each process [7]. Figure 3 shows that higher toughness is generally achieved with GTAW, PAW and GMAW than with SMAW, SAW and FCAW. The results on SMAW and SAW with proper welding procedures are generally acceptable for meeting requirements for toughness testing at –40 °C (–40 °F), such as in ASTM A923. FCAW may not pass these toughness requirements, but is not yet widely used for DSSs in refinery process services. FCAW is widely used for welding of thin-wall components in the flue gas desulfurization (FGD) and desalination industries, and the thinner welds can typically achieve acceptable toughness.

ASME Section VIII requirements for impact testing for DSS base and weld metals are given in UHA-51(d)(3)(a), which requires testing of all DSSs thicker than 10 mm ($^3/_8$ in.) or those with an MDMT less than –29 °C (–20 °F). ASME B31.3 requires testing of welds when the MDMT is less than –29 °C (–20 °F) and of base metals when the MDMT is below the minimum allowable temperature for the specific grade.

Maximum operating temperatures are limited by the susceptibility of the ferritic phase to 475 °C (885 °F) embrittlement (see 5.7) and other embrittlement mechanisms. Most Codes applicable to refinery equipment and piping limit the various DSS grades to between 260 °C to 340 °C (500 °F to 650 °F), maximum, to avoid these problems (Table 5). Welds are more prone to sigma formation than base materials, and hence, these temperature limits are especially important with welded components.

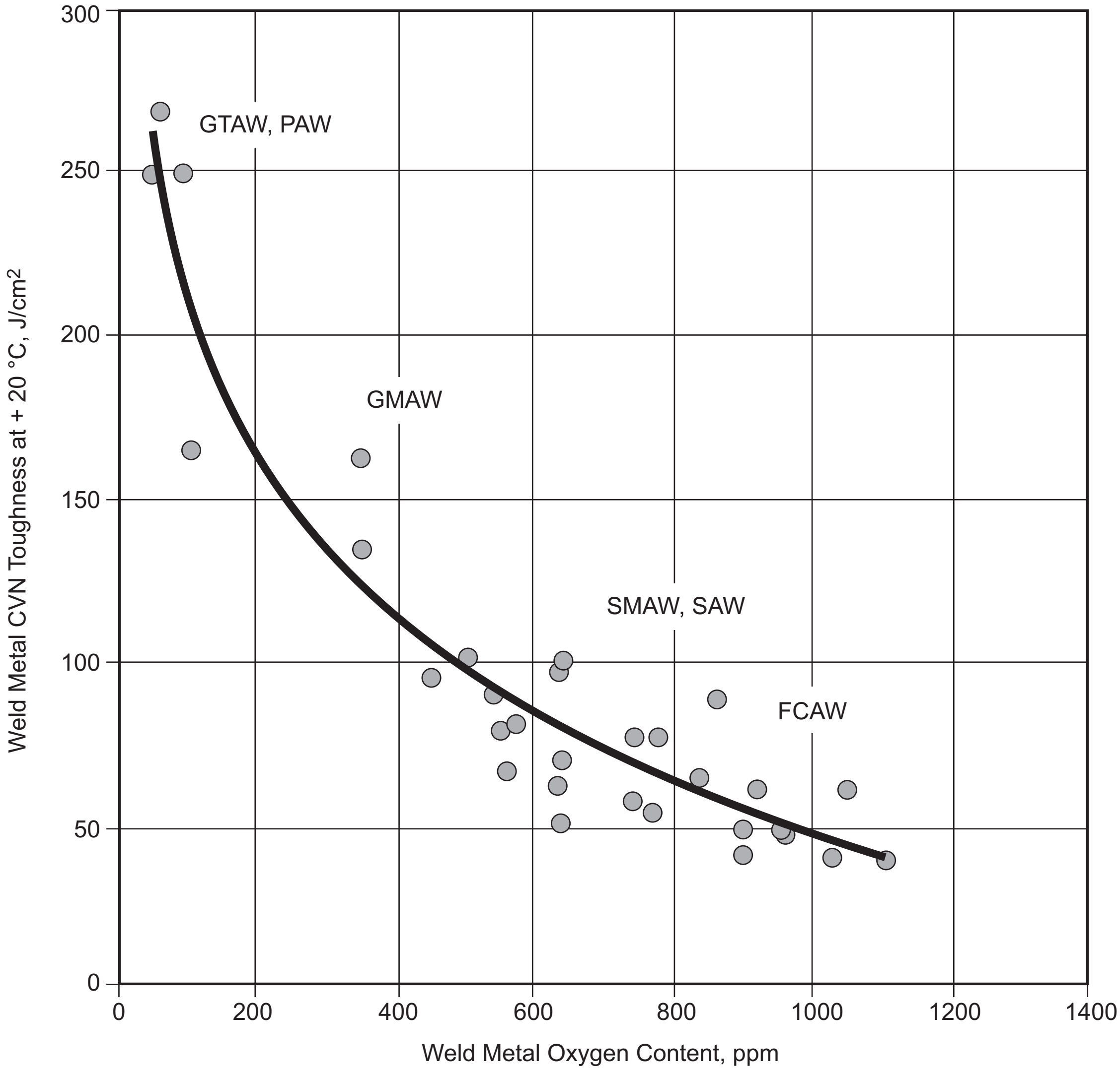


Figure 3—Effect of Weld Metal Oxygen Content on the Toughness of the Weld [7]

4.5 Hardness Conversions

The hardness conversions between the Rockwell C, Vickers and Brinell scales are different for DSSs as compared to CS and other low-alloy, ferritic steels [2]. This is an important consideration when hardness limits from industry standards in Rockwell C are applied to weld procedure qualifications, which are typically testing using a Vickers method. The conversion chart given in ASTM E140 is often used, even though this chart was developed for CS and low-alloy steels. It results in a conservatively low Vickers criteria for DSSs. This effect is shown by the curves in Figure 4. For example, for a desired limit of HRC 28, CS should use 286 HV, while DSSs should use 334 HV. Also relevant for microhardness measurements is the possibility that the size and orientation of the two phases may be coarse relative to the indenter size in certain products, such as cast DSSs.

Vickers hardness is the most practical and accurate hardness testing method for DSS welds, but the method of preparation of the sample and the load used for the testing can strongly affect the results. Low loads are particularly necessary for accurate measurement of HAZ hardness.

Table 5—ASME Code Maximum Allowable Temperatures

Grade	ASME Section VIII (Div. 1) °C (°F)	ASME B31.3 °C (°F)
S32304	316 (600)	316 (600)
S32101	316 (600) Code Case 2418	NL
S32202	316 (600)	NL
S32003	343 (650) Code Case 2503	343 (650)
S82011	343 (650) Code Case 2735	NL
S82441	316 (600) Code Case 2780	NL
S31803/S33205 (Note 1)	316 (600)	316 (600)
S32550	260 (500)	NL
S32750	316 (600)	316 (600)
S32760	316 (600)	316 (600)
S32906	316 (600)	NL
S32707	260 (500) Code Case 2586	NL

NOTE 1 NL = not listed.

NOTE 2 S32205 can use the design allowables for S31803 if the material is dual-certified.

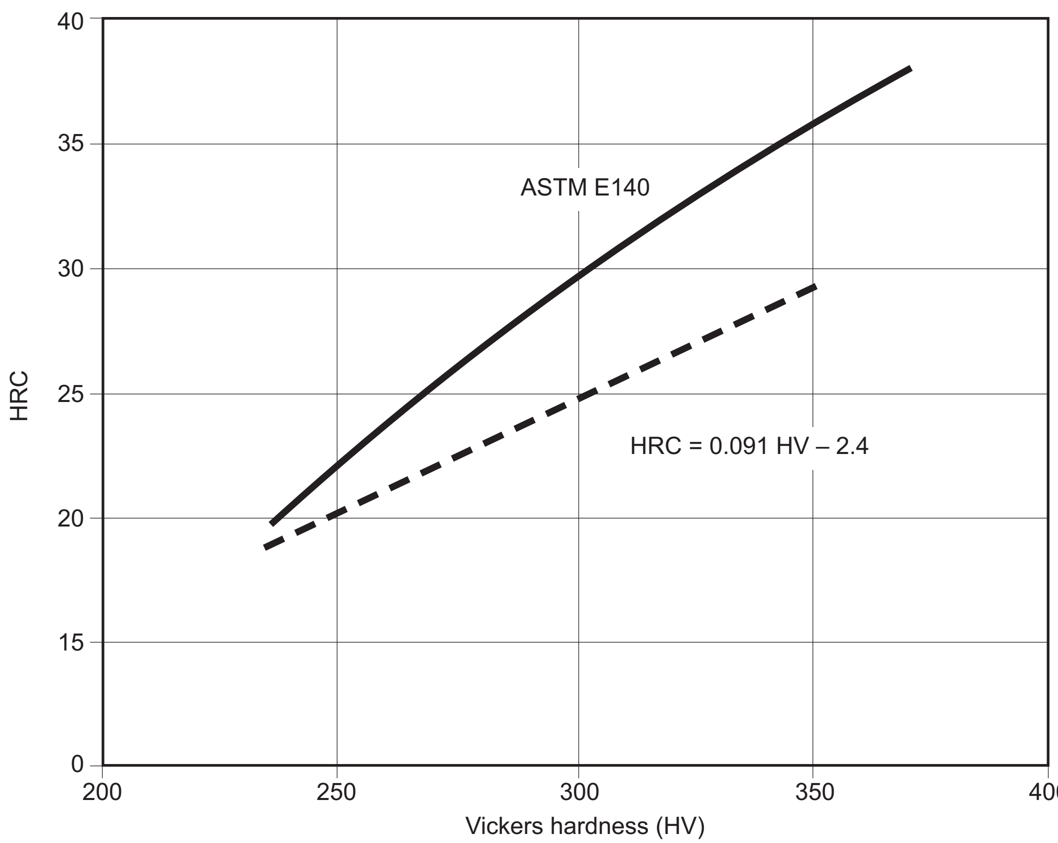


Figure 4—Compilation of Hardness Data for a Range of Duplex Parent Materials and Weldments Showing the Best-fit Line and ASTM E140 Conversion for Ferritic Steel [2]

5 Potential Environment-Related Failure Mechanisms

5.1 Chloride Pitting and Crevice Corrosion

Because DSSs are generally designed with higher Cr levels than the austenitic stainless grades, and because the duplex grades readily accept alloying with molybdenum and nitrogen, various DSSs grades have significantly better chloride pitting and crevice corrosion resistance than the standard austenitic SS, such as 304L and 316L (UNS S30403 and S31603). The most common tools for predicting the chloride pitting resistance of corrosion resistant alloys are the PREN and CPT. The PREN is a statistical regression relationship based on the effect of composition on CPT in a particular test environment, such as ASTM G48, for many commercial grades. The PREN correlates the chloride pitting resistance provided by the contributing elements in the alloy composition, namely chromium, molybdenum, nitrogen, and tungsten, as long as the elements are present in a "balanced" composition, as reflected in the established grades. Two commonly reported equations are given below. There are several variations reported in the literature, however, the following are the most prevalent (with the second formula being used by many industry standards including, NACE MR0175/ISO 15156).

$$\text{PREN} = \%\,\text{Cr} + 3.3 \times \%\,\text{Mo} + 16 \times \%\,\text{N}$$

$$\text{PREN} = \%\,\text{Cr} + 3.3 \times (\%\,\text{Mo} + 0.5 \times \%\,\text{W}) + 16 \times \%\,\text{N}$$

While PREN is useful in roughly ranking alloys, other material factors may play a role in the chloride pitting resistance, such as the surface finish, welding quality, and other fabrication details. In addition, with DSSs (especially for grades with an overall PREN less than about 40), the two phases will have partitioning of the alloying elements, and hence, can have a different PREN for each phase. For most DSSs material from experienced suppliers, this has not been a significant problem as these suppliers strive to balance the PREN between the two phases. In standard duplex SS grades, the austenite grains can have a lower PREN, and in the lean duplex SS grades, the ferrite grains can be lower PREN compared to the PREN based on overall chemistry. In some severe services, such as some flue gas desulfurization units, this has led to selective attack of the phase with the lower PREN. Some examples of alloy partitioning for 25 Cr DSSs are shown in Table 4 and Table 8, which are part of 4.2 and 5.6 of this report, respectively.

Service factors affecting the aggressiveness of chloride pitting environments include temperature, chloride concentration, oxygen content, other oxidizing species, and pH. One of the most common tests for determining the CPT is the ASTM G48 Test Method E (formerly ASTM G48 Test Method C) test, which is run in an acidified aqueous solution of ferric chloride having about 6 % $FeCl_3$ by mass and about 1 % HCl. Results of ASTM G48 CPT tests in ferric chloride on various duplex and austenitic SS grades are shown in Figure 5 [8] and Figure 7 [9]. Figure 6 shows the critical pitting temperatures at various concentrations of sodium chloride at neutral pH for 304L, 316L, UNS S32304 and UNS S32205 [8].

One test program targeted for the refining industry measured the resistance of various alloys to 20 wt.% and 40 wt.% ammonium chloride solutions and it showed excellent resistance of Super DSS with a PREN of 40 or higher [9]. However, a second test program showed pitting of Super DSS under an ammonium chloride salt deposit when the relative humidity was 50 % and 60 % (the testing was done at 80 °C). This test program also studied the critical relative humidity (CRH) of ammonium chloride salt deposits at different temperature, which also had an effect on the corrosion [10].

Crevice corrosion resistance is similarly shown by a CCT that is commonly determined by ASTM G48 Test Method F (formerly ASTM G48 Test Method D) test. This test gives lower temperature results, which indicate that it is a more severe test. Figure 7 shows CCT results on duplex and austenitic SSs. The CCT is a function of the severity of the crevice, including the selection of the crevice forming material.

Corrosion under insulation (CUI) is due to wet insulation forming aqueous chloride-containing solutions on the metal surfaces. These conditions can cause corrosion on carbon steel, austenitic SS or DSS, and chloride stress corrosion cracking (SCC) on austenitic SS or DSS. NACE SP0198, "Control of Corrosion Under Thermal Insulation and Fireproofing Materials—A Systems Approach" addresses this concern and gives recommended coating systems.

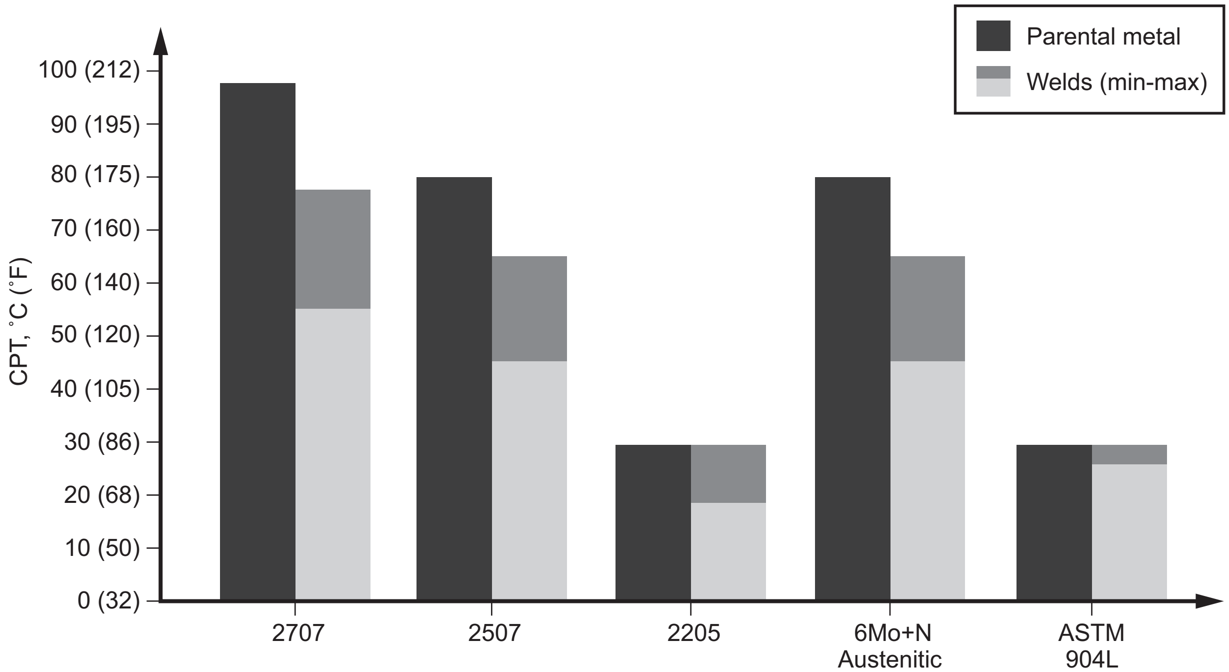


Figure 5—CPT for 22 % Cr, Super and Hyper DSSs Alloys Compared to Austenitic SS Alloys in 6 % $FeCl_3$, ASTM G48 Test Method A [8]

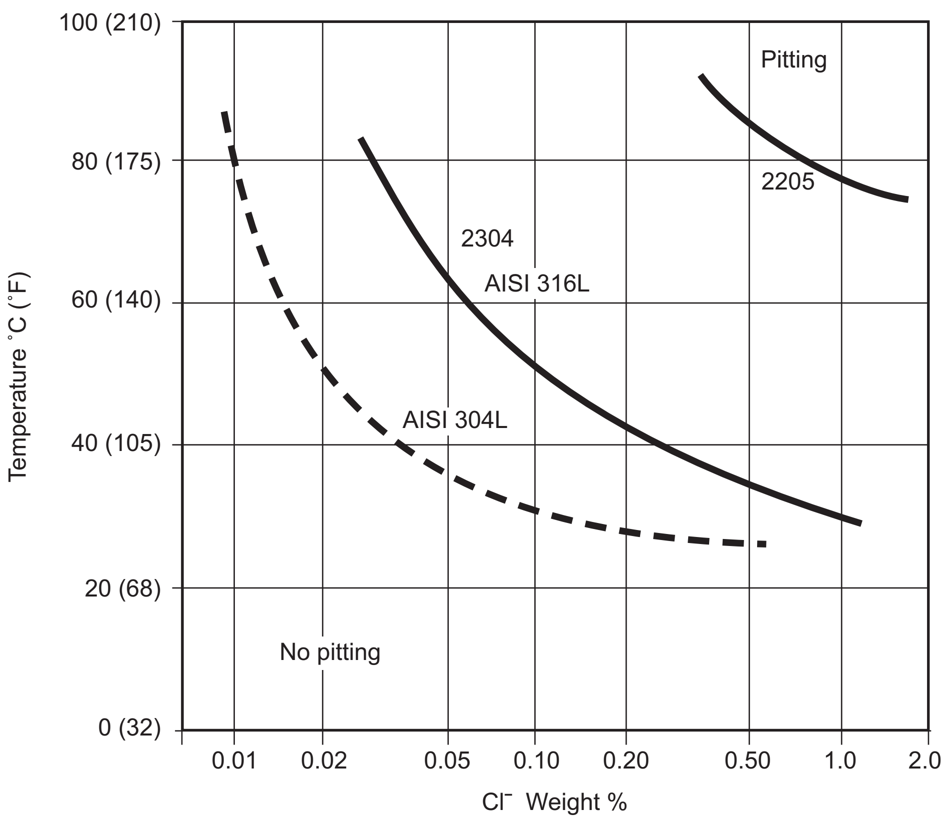
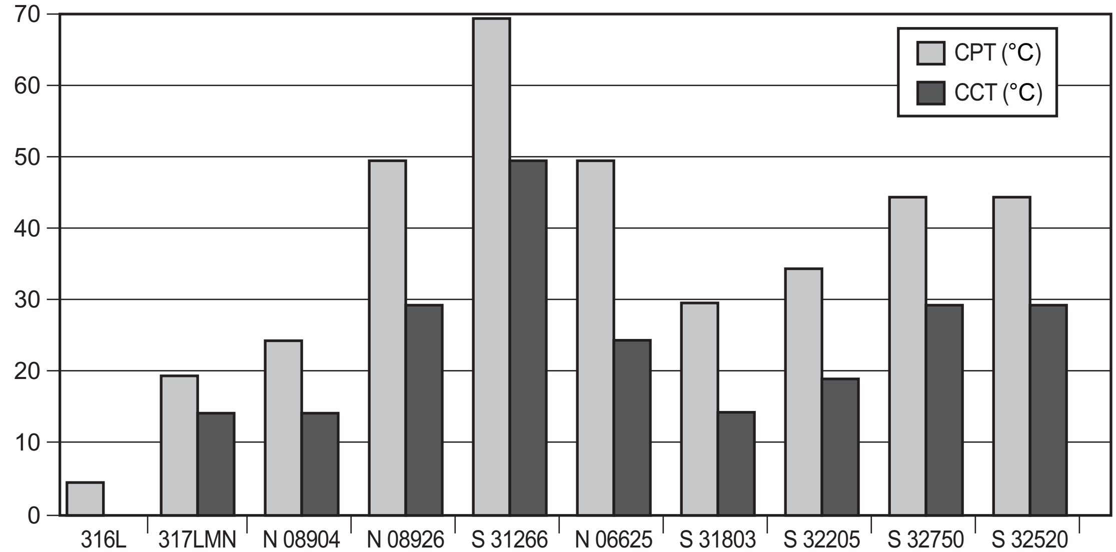


Figure 6—CPTs at Various Concentrations of Sodium Chloride (at +300 mV vs. SCE, Neutral pH) [8]



NOTE 27 % Cr Hyper DSS is reported to have a minimum CCT of 70 °C based on ASTM G48 testing [11], [12] .

Figure 7—CPTs and CCTs for 22 % Cr and Super DSSs Compared to Austenitic SS Alloys in ASTM G48 Tests

Duplex SS is more resistant than austenitic SS to corrosion and SCC, but not immune as shown by the following excerpt from NACE SP0198:

> "The higher-nickel, chromium, and molybdenum-containing austenitic stainless steel alloys and the lower-nickel, higher-chromium duplex stainless steel alloys have been found to be more resistant to SCC under thermal insulation, but are not immune. For example, recent offshore experience found that under severe conditions, duplex stainless steels also can suffer from external SCC under insulation. Protective coatings and systems may be used to mitigate the threat associated with CUI of austenitic and duplex stainless steels."

Hence, DSS components which are insulated and in an area where the climate or atmospheric conditions and temperature range create a risk of external chloride SCC, are typically protected by coating, using thermal spray aluminum (TSA) or wrapping with foil in a similar manner as specified for austenitic SS. Other industry standards, including some in Europe, are also adopting similar requirements.

5.2 Corrosion in Seawater

Although all the variables mentioned in 5.1 are important factors for corrosion resistance in seawater, there are rules-of-thumb that have been developed. Experience has shown that SS typically need a PREN ≥40 to resist pitting and crevice corrosion in ambient temperature seawater. Seawater corrosion is a highly complex situation where aeration, filtration, biofouling and biofouling control, and salinity lead to corrosion behavior that is not necessarily directly proportional to temperature. This makes the acceptability of 22 % Cr DSSs difficult to predict, hence, 25 % Cr Super DSSs that meet the minimum PREN of 40 are more commonly used in seawater-cooled heat exchangers. 27 % Cr Hyper DSS can be used in seawater applications at higher temperatures than Super DSSs.

The super and hyper duplex SS grades (PREN ≥40) have shown excellent resistance to general and localized corrosion in polluted and unpolluted seawater. They can also be considered to have good resistance to stress corrosion cracking in seawater service (see Section 5.3). These alloys also possess good erosion resistance in seawater heat exchanger tubing applications when exposed to fluid velocities up to 10 m/s (32.8 ft/s).

It is common practice that seawater cooling water is chlorinated to control biofouling. Chlorination increases the corrosion potential that causes localized corrosion attack. The maximum tube metal temperature limit for duplex SS grades is lower with chlorinated seawater than in natural seawater.

Seawater also has normally a high amount of dissolved calcium and carbon dioxide that respects the chemical equilibrium below:

$$Ca^{2+}(aq) + 2HCO_3^-(aq) \leftrightarrow CaCO_3(s) + CO_2(g) + H_2O$$

Very often it is only the seawater that comes into contact with the hot tube wall that reaches sufficient temperatures to cause corrosion. At approximately 60 °C (140 °F), seawater begins to decompose, driving CO_2 from the system and pushing the chemical equilibrium to the right, thus precipitating $CaCO_3$. The higher temperatures under the $CaCO_3$ deposits can lead to the deposition of sulfates, carbonates and other salts on the tube wall. If the higher temperature approaches the boiling point, chloride salts can also deposit giving a very aggressive set of conditions. These deposits and high temperatures can lead to a risk of crevice/underdeposit corrosion within a short time after their formation.

In a modified version of ASTM G48A, test samples are exposed for periods of 24 hours in 6 % $FeCl_3$. This solution has a corrosion potential of +600 mV that is equivalent to continuously chlorinated seawater's potential. When pits are detected together with a substantial weight loss (> 5 mg), the test is interrupted. Otherwise, the temperature is increased 5 °C (9 °F) and the test is continued. The CPT of S32707 defined in this way was 97.5 ˚C (207.5 °F), compared to approximately 80˚C (176 °F) for S32750 [11], [12].

A typical limit for Super DSS (with PREN ≥40) heat exchanger tubing in seawater is 60 °C (140 °F) at flow velocities of 1.5 m/s (5 ft/s), minimum. However, if there is a risk of deposits or if the seawater is chlorinated, the limit is suggested to be reduced to 50 °C (120 °F). An additional requirement is that incoming seawater should be filtered in order to reduce silt and sand deposits that promote corrosion. However, the calcium carbonate fouling described above cannot be prevented by filtration or maintaining flow rates and hence, is typically the defining factor when it comes to using super duplex and other stainless steels in chlorinated seawater cooling applications. For seawater-cooled heat exchangers working with metal temperatures above this critical temperature of 60 °C (140 °F), there is a risk of underdeposit corrosion. Hyper DSSs show improved resistance and are being used in some cases up to 70 °C (160 °F), with or without continuous chlorination [11].

5.3 Chloride Stress Corrosion Cracking (CSCC)

The risk of CSCC restricts the use of standard austenitic SS grades, such as 304L and 316L, based on chloride concentrations, temperatures and various other factors. Depending on the chloride concentration in the bulk solution along with consideration of concentrating mechanisms (such as hot surfaces, underdeposits or crevices), actual metal temperature, acidity/pH, tensile stress, time of exposure, and oxygen content, CSCC can cause rapid failures. In most cases, temperatures greater than 60 °C (140 °F) are a risk for cracking of those austenitic SS grades, with cracking tendency increasing with increasing metal temperature. However, the risk of CSCC is dependent upon all of the listed factors, and in severe cases, CSCC can occur at slightly lower temperatures.

DSSs are a common "replacement" or alternative material in services where the threat of CSCC makes 300 series SSs a poor or marginal alloy choice. Practical experience and laboratory testing have shown DDSs to have good resistance to CSCC, but they are not immune [8], [13]. Figure 8 and Figure 9 present results of tests that compared various grades of DSSs with other alloys in chloride solutions. Results from high-pressure autoclave tests in neutral, oxygenated chloride solutions are shown in Figure 8 [8]. The tests indicate the comparative cracking thresholds versus chloride concentrations and temperatures for various alloys.

Figure 9 shows the results of constant-load tests in an aerated, 40 % calcium chloride solution, acidified to a pH of 1.5 at 100 °C (212 °F) [8]. Time to failure is shown as a function of the loading level. The results show that the DSSs have a much higher resistance to SCC under these conditions than does austenitic SS.

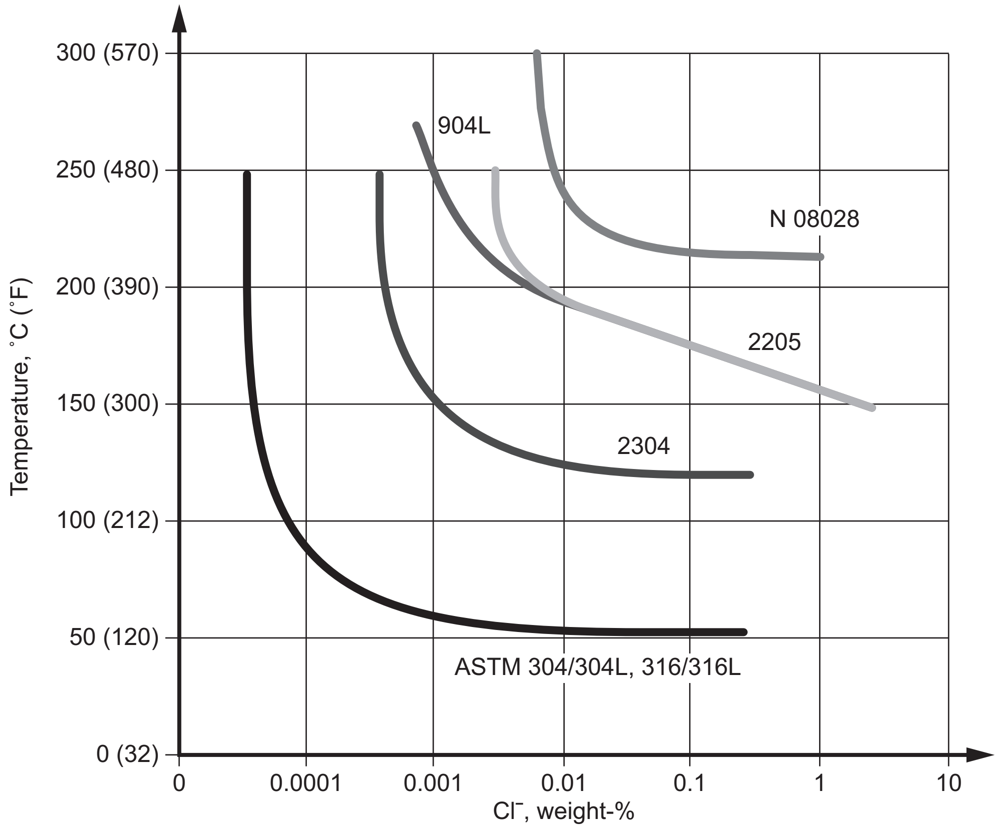


Figure 8—CSCC Resistance of DSSs Alloys Compared to Austenitic SS Alloys in Oxygen-bearing Neutral Chloride Solutions [8]

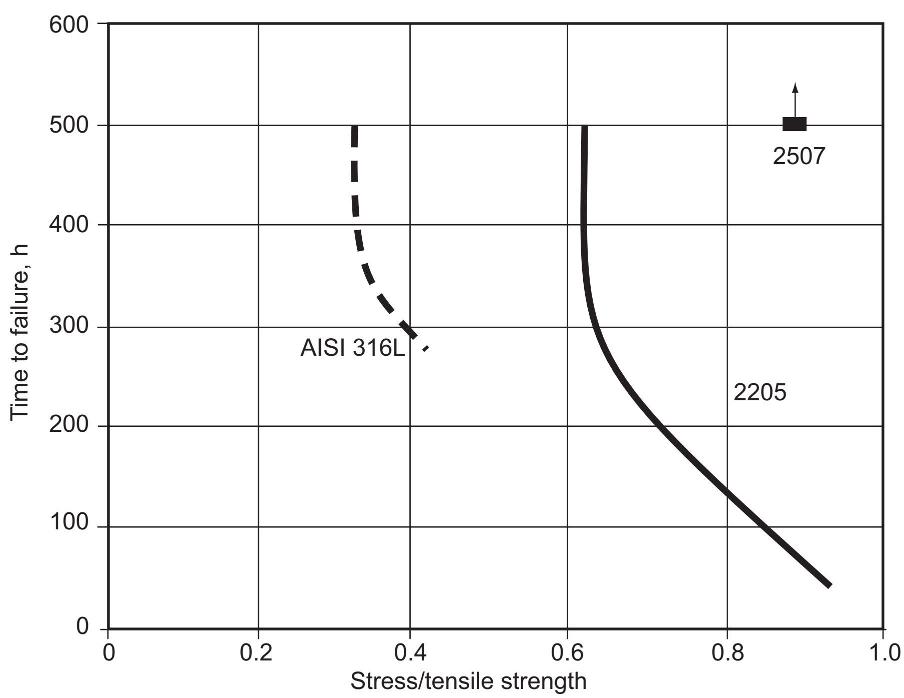


Figure 9—Results of SCC Tests of 22 % Cr and 25 % Cr DSSs Alloys Compared to Austenitic SS Alloys in Constant Load Tests in 40 % $CaCl_2$, 1.5 pH at 100 °C with Aerated Test Solution [8]

Additional considerations for predicting susceptibility of a DSS to CSCC include the following.

a) Chloride concentration can build up under boiling conditions, in the water film in contact with a heat-rejecting surface, under deposits or in a crevice. Cases of CSCC have occurred on Standard and Super DSSs which were exposed to chloride salt deposits, resulting in extremely high localized chloride concentrations, and some of these cases were at surprisingly low temperatures [14], [15], [16], [17], [18]. The various types of chloride salts (such as Na, Mg, Ca, Fe, NH_4, Li, etc.) also showed variations in severity.

b) High pH environments, such as those containing NH_4HS (ammonium bisulfide), amine, or caustic, are expected to have higher thresholds for CSCC than neutral or acidic solutions.

c) Wet-dry conditions, as may occur when water drips on a hot metal surface, can be especially aggressive because of localized thermal fatigue and/or crevice corrosion originating CSCC from the deposits formed as the water evaporates (in some cases external coatings have been recommended on duplex SS components exposed to seawater splashing which operate above 100 °C (212 °F) [19].

d) H_2S may interact with chlorides to cause greater susceptibility to cracking, especially in acidic pH conditions, but these interactions are still under investigation.

There have been a few reported cases of cracking in the industry, but most were under severe conditions where SCC could be predicted. Some of those examples have occurred in offshore facilities and were attributed to external SCC on relatively hot equipment. One case of internal CSCC on an offshore platform occurred on 22 % Cr DSSs after only a few weeks of service. The conditions were 200,000 ppm to 460,000 ppm Cl, pH 3.4, 140 °C (284 °F) and no oxygen (<1 ppb). There is one example of CSCC of a 25 % Cr DSSs in a crude unit application with chloride salt deposits shown in Table 11, and other examples of CSCC from refinery services reported in NACE Refin-Cor are summarized in Table 10 (these tables are part of Section 8 in this report).

CUI can also lead to corrosion or CSCC of DSSs, as discussed in 5.1 of this report.

5.4 Hydrogen Stress Cracking (HSC)/Sulfide Stress Cracking (SSC)

Many services where DSSs are used in refineries involve a water phase containing H_2S, and hence, there is a risk of HSC.

The behavior of DSSs with H_2S aqueous solutions is dependent on the type of sulfur present in the environment. In the water phase, there is a balance of H_2S, HS^- and S_2^-, as a function of the pH. The reactions for each pH level are described below:

$$Fe + H_2S = FeS + 2H^+ \text{ (acid pH)}$$

$$Fe + HS^- = FeS + H^+ + 2e \text{ (neutral pH)}$$

$$Fe + S_2^- = FeS + 2e \text{ (basic pH)}$$

One form of HSC is sulfide stress cracking (SSC), which can occur in high-strength (hard) zones of base materials or welds. SSC susceptibility is dependent on many variables: partial pressure of H_2S, pH, chloride content, temperature, microstructure, hardness, cold work, surface finish, etc. In the NACE TM0177 test for SSC, most DSSs do not show any cracking until the applied stress is well above the proof strength. Cold work decreases the threshold failure stress.

Numerous fabrication requirements can be specified to minimize hardness and hence, susceptibility to these cracking mechanisms. There has also been extensive testing done on DSSs resistance at acidic pHs to understand and avoid this cracking. Although there is controversy on the test methods and the ability to compare results between different test programs or to service conditions, the results have allowed some limits to be established on the use of different alloys. Note that the conditions in wet sour environments in oil production generally vary from those in refining. Production environments typically also contain carbon dioxide and bicarbonate ions and are lower than neutral pH, while many of the applicable refining environments contain high amounts of ammonia, and are higher than neutral pH. Also, production environments often contain significantly higher levels of chlorides.

For solution annealed DSS materials, NACE MR0175/ISO 15156 gives varying PREN, temperature, H_2S partial pressure, and ferrite content limits (35 % to 65 % for wrought and cast materials, and 30-70% for welds), with any chloride levels required for different grades of DSSs to prevent SSC. For these cases, it does not require a hardness limit for the services within its scope. The process limits were developed specifically for the oil and gas production industry, and were based on experience and laboratory testing focused on producing environments. Refining environments have significant differences in pH, other contaminants, etc., and hence, the NACE MR0175 limits are not always applicable. Refining applications of DSSs have often exceeded, and sometimes significantly, the H_2S partial pressure limits in NACE MR0175, and the DSSs have provided good resistance.

A separate table in NACE MR0175/ISO 15156 applies to cold-worked DSS materials, but the title of the table indicates that it applies only to “downhole tubular, packers or other subsurface components”. For DSSs with various PRENs, limits are given on H_2S partial pressure, and in some cases, chloride contents, in addition to a hardness limit of 36 HRC, maximum. Some users in the production industry reportedly apply this table to additional cold worked components besides those listed in the table title.

Additional research is being done in oil and gas environments to possibly raise the NACE MR0175/ISO 15156 limits, but this research may not be directly applicable to many of the high pH SSC environments in refineries. Table 6 and Table 7 present data from recent papers [20], [21].

A second NACE standard is MR0103, which is similar to older versions of NACE MR0175, but is targeted for the refining industry. It limits DSSs base materials in severe wet sour services to 28 HRC maximum hardness for PREN ≤40 and 32 HRC for PREN >40. For the weld procedure qualification, it specifies that the average hardness shall not exceed 310 HV and no individual reading shall exceed 320 HV. Additional research is needed on this topic to optimize these hardness limits in refining services.

Some SSC failures in refinery applications have been attributed to improper fabrication which led to ferrite contents and/or hardnesses in some zones of the weldment being outside of specified limits. The suggested hardness limit of 310 HV, average (320 HV max), for Standard DSS weld procedure qualification given in API 582 for S31803/S32205, along with the tight control of welding variables helps ensure that the production welding matches the qualified procedures, which are the primary means of minimizing the risk of HSC/SSC. Super and Hyper DSSs require a higher hardness limit due to their higher yield strength and testing indicates they are acceptable to higher values.

Table 6—Estimated H_2S Partial Pressure Limits for DSS in Production Services Based on Literature, Laboratory and Experiential Data (KPa [psi]) [20]

	22 % Cr DSS		25 % Cr Super DSS	
Chlorides	**pH 3.5**	**pH 4.5**	**pH 3.5**	**pH 4.5**
1000 ppm	50 (7.25)	>200 (29.0)	70 (10.15)	>200 (29.0)
10,000 ppm	30 (4.35)	200 (29.0)	50 (7.25)	>200 (29.0)
100,000 ppm	20 (2.90)	30 to 40 (4.35 to 5.80)	30 (4.35)	80 to 100 (11.6 to 14.5)

NOTE 1 This table is applicable to solution annealed materials.

NOTE 2 These limits have not been confirmed for welds.

NOTE 3 The variables of temperature and applied stress are considered to be “incorporated” and these limits encompass all practical ranges for wet sour applications at these pH ranges, which meet design codes.

NOTE 4 Higher pH (>8 or 9) refinery services may not be represented by this data.

Table 7—Successful Service Experience with DSS in Production Sour Services [20]

DSS Grade	H_2S PP [Kpa (psi)]	Temperature (°C)	pH	Chlorides (ppm)	Duration (years)
22 % Cr	25 (3.63)	80	6	8,000	8
22 % Cr	~1000 (145.0)	60 to 110	4.5	20 to 50,000	>3
22 % Cr	~400 (58.0)	40 to 60	3.7	<100	>10
22 % Cr	160 to 500 (23.2 to 72.5)	40 to 60	3.5	<100	>5
22 % Cr	75 (10.9)	50 to 80	4.7	25,000	6
25 % Cr	5.0 (0.73)	<200	3.5	175,000	10
25 % Cr	125 (18.1)	<125	4.2	25,000	6

In 2011 through 2013 about seven cases of weld cracking were reported in hydroprocessing unit REAC services. They were in some of the most severe refining environments with high NH_4HS concentrations, high pressures and high H_2S partial pressures. The thickness at the welds were generally >25 mm (which resulted from the high pressure service). Some cases were attributable to poor fabrication and were confirmed to have high hardness and/or high ferrite contents in the weld or HAZ, which then led to SSC cracking. However, in other cases equipment seemed to be fabricated using good industry practices [22]. These cases have been added to Table 11 and are currently under further investigation (primarily by the Materials Technology Institute in a 2013-2014 program) with the objective of developing additional fabrication and/or non-destructive testing (NDE) steps applicable to thick-wall duplex SS air coolers and other components to help ensure their resistance to SSC and NH_4HS corrosion in these environments.

5.5 Ammonium Bisulfide Corrosion

There is some laboratory data showing the resistance of DSSs to ammonium bisulfide environments [23], [24], and extensive experiential data as shown by the examples included in Table 10 and Table 11 [25]. Case histories come from hydroprocessing, sour water strippers, FCC and coker units. Duplex 2205 is one of the commonly-used alloys for REACs under relatively severe conditions and was shown by an extensive testing program to be just slightly below Alloy 825 in NH_4HS (ammonium bisulfide) corrosion resistance. Super DSS was shown to have resistance slightly superior to Alloy 825 and Alloy 625, and just slightly below Alloy C-276 [24]. Another good reference on the use of DSSs in REACs is API 932-B.

There are numerous case histories of DSSs applications in hydroprocessing units with NH_4HS concentrations up to 10 %. However, it is important to consider that there are other critical variables affecting the acceptability of, and threshold NH_4HS concentration for DSSs, including velocity (shear stress), H_2S partial pressure, temperature, water injection distribution and contacting, water quality, chlorides, etc. A proprietary joint research program was sponsored by interested companies to collect data on NH_4HS corrosion. The program was initiated in March 2000 and concluded the initial phase of work in February 2003, and second and third phases shortly after [26]. Results of this work have better defined the roles of several key variables on corrosion behavior, and developed a software program called Predict-SW, which gives predicted NH4HS corrosion rates for various materials [24]. Some new applications have used 9.1 m/s (30 ft/s) as the maximum velocity for Standard DSSs; however, this limit may be conservative in many cases.

One case of DSS failing due to NH_4HS corrosion in a sour water stripper (SWS) is listed in Table 10; however, the NH_4HS concentration was not reported. The environment in SWSs is different than in REACs, as SWS environments are low pressure, do not have hydrocarbons, can have greater NH_3 than H_2S (in partial pressures), can have NH_4HS concentrations up to 25 %, etc. The Predict-SW software mentioned above also gives guidance for SWS environments [24].

Recent reported SSC failure cases of duplex heavy wall (>25 mm [1 in.]) welded REACs have occurred on welds that did not show obvious signs of improper fabrication. Further study is being done on these failures to optimize the specifications for thick wall fabrication. Additional discussion on these failures and concerns is given in the previous section of this report and they are listed in Table 11.

In air coolers (especially REACs) with a risk of wet ammonium chloride salt deposits, DSSs could be susceptible to chloride pitting, as discussed above in 5.1. These deposits are extremely corrosive to almost all alloys, and hence, the deposit formation should be prevented by process measures, such as water washing or maintaining a minimum temperature, rather than attempting to prevent corrosion with metallurgy [26]. The presence of cyanides at levels above about 20 ppm can also greatly increase the risk of NH_4HS corrosion on almost all alloys, except the nickel-based alloy C family. DSS piping has shown cyanide-related NH_4HS corrosion in a Sour Water Stripper overhead with 80 ppm to 90 ppm cyanides [27].

5.6 Naphthenic Acid Corrosion

Naphthenic acid corrosion occurs primarily in crude units due to organic, carboxylic acids in the crude oil and distilled cuts. The temperature range where it occurs is approximately 175 °C to 425 °C (350 °F to 800 °F), and the primary variables affecting the corrosion rates are organic acid concentration, temperature, velocity, and sulfur content and species. Molybdenum content is important for naphthenic acid corrosion resistance and alloys with 2.5 % minimum Mo provide acceptable corrosion resistance in most cases.

There are little or no published laboratory data and minimal documented experiential data for DSSs in naphthenic acid refining services. One case alleged the successful use of SDSS, grade S32707, in a crude preheater which was known to encounter conditions which could cause naphthenic acid corrosion. Also, based on the numerous times DSS has been specified for this service, there are probably many other recent applications currently in service. Some industry materials experts believe DSS grades with ≥2.5 % Mo to have good naphthenic acid corrosion resistance based on their alloy content, however, partitioning on the molybdenum between the austenitic and ferritic phases needs to be considered, as discussed below.

In most areas susceptible to naphthenic acid corrosion, 317L austenitic SS which has a specified Mo content of 3 % to 4 % has displayed excellent resistance, but there are some services where 317L SS has not performed adequately or is deemed undesirable. Examples are heat exchanger tubing with a hot, naphthenic stream on one side and either un-desalted crude, crude tower overhead or steam generating on the other side. 317L SS, although resistant to naphthenic acid corrosion, would have risks of CSCC from the other side's service. DSSs will have superior CSCC resistance, as discussed in 5.3, but would be limited to 260 °C to 340 °C (500 °F to 650 °F) design temperatures based on Code limits (shown in Table 5).

Partitioning of the molybdenum between the two phases of DSSs could affect the overall naphthenic acid corrosion resistance. Early papers on DSS alloy development showed that the partitioning results in a ratio of 1.5 to 1.6 for Mo in the ferrite to austenite phases [2], [4]. This means that the austenite phase may have as low as 38.5 % of the "bulk" Mo content. Table 8 depicts some examples of partitioning in various DSS alloys and welds.

5.7 475 °C (885 °F) Embrittlement

Prolonged exposures at above 260 °C to 340 °C (500 °F to 650 °F) depending on grade, may initiate embrittlement in DSSs. This phenomenon is most rapid at about 475 °C (885 °F), hence, it is known as "475 °C embrittlement." The mechanism causing the embrittlement is decomposition of the ferrite into a brittle, Cr-rich alpha prime phase. This is the primary reason that the Code temperature limits are in the 260 °C to 340 °C (500 °F to 650 °F) range and indicates that the DSSs should not be used for long durations above the Code limits.

The susceptibility to degradation of the base materials due to short-term exposures is shown in Figure 10 and Figure 11 [2], [4]. The 25 % Cr and 27 % Cr alloys are more susceptible to this embrittlement than are UNS S32205 or S32304, and they can embrittle from a room temperature toughness level of >150 J (111 ft-lb) to 27J (20 ft-lb) from 10 hours of exposure to 475 °C (885 °F). Similar levels of embrittlement would take >10,000 hours at 300 °C (570 °F). This embrittlement will also occur more rapidly in weld metals than in base material.

Table 8—Partitioning of Alloying Elements Between Phases

A—In 25 % Cr Alloys [27]

Sample	Phase	Phase Volume %	Cr (wt. %)	Ni (wt. %)	Mo (wt. %)	Fe (wt. %)	N (wt. %)	PREN
1 [a]	Austenite	65	24.5	8.3	2.9	Bal.		
	Ferrite	35	29.3	3.9	4.3	Bal.		
2 [a]	Austenite	65	25.4	8.5	3.3	Bal.		
	Ferrite	35	29.3	4.8	5.0	Bal.		
3 [b]	Austenite		23.5	8.2	3.5		0.48	42.7
	Ferrite		26.5	5.8	4.5		0.06	42.3

[a] Estimated volume fraction of phases determined by backscattered SEM analysis. Chemical composition analysis of phases determined by STEM/EDS analysis (nitrogen cannot be obtained using this testing equipment).

[b] Chemical composition and PREN numbers of individual phases of 25-7-4 quench-annealed at 1075 °C (1967 °F).

B—In 22 % Cr Weld Metals (Approx. Wt. %) [28]

Weld Metal Type	Phase	Cr	Ni	Mo	N	PREN
22 Cr-10 Ni-3 Mo-0.12 N	Austenite	20 to 21.5	10.5 to 11.5	2.5 to 3	0.2 to 0.5	31.5 min
	Ferrite	22 to 23.5	8.5 to 9.5	3 to 3.5	< 0.05	32 min
22 Cr-6 Ni-3 Mo-0.12 N	Austenite	21 to 24	5.5 to 8	2.5 to 3.5	0.3 to 0.6	34 min
	Ferrite	21 to 24	5.5 to 8	2.5 to 3.5	< 0.05	29 min
22 Cr-6 Ni-3 Mo-0.18 N	Austenite	21 to 22	6 to 8	2.5 to 3	0.3 to 0.6	34 min
	Ferrite	22 to 24	5 to 6	3 to 4	< 0.05	32 min

C—In 22 % Cr Base Metal and SMAW Weldments with Varying Arc Energy (Wt. %) [28]

Weld Region	Phase	Cr	Ni	Mo
Parent Steel	Austenite	19.5	7.0	2.4
	Ferrite	23.2	4.1	3.3
As-deposited Root [a]	Austenite	23.7	7.8	2.8
	Ferrite	23.9	7.5	3.0
Reheated Root [a]	Austenite	23.4	7.7	2.7
	Ferrite	23.7	7.2	3.0
As-deposited Root [b]	Austenite	23.7	7.7	2.5
	Ferrite	23.8	7.2	2.7
Reheated Root [b]	Austenite	22.7	8.6	2.5
	Ferrite	25.1	6.2	3.7
As-welded HAZ [b]	Austenite	21.3	5.7	2.7
	Ferrite	21.3	5.6	2.9
Reheated HAZ [b]	Austenite	20.9	5.9	2.9
	Ferrite	21.9	5.2	3.4

[a] Root and fill passes at 0.7 kJ/mm.

[b] Root at 0.5 kJ/mm, fill passes at 3.2 kJ/mm.

D—In 22 % Cr Base Metal and GTAW Weldment (Wt. %) [28]				
Weld Region	**Phase**	**Cr**	**Ni**	**Mo**
Unfilled Weld Root	Austenite	22.2	6.9	2.7
	Ferrite	22.4	6.2	3.1
Reheated Weld Root	Austenite	22.1	7.4	2.8
	Ferrite	22.7	6.6	3.3

E—In 22 % Cr DSS Base Metal			
	Cr	**Ni**	**Mo**
Austenite Grain 1	20.90	6.64	2.48
Austenite Grain 2	20.09	6.99	2.22
Austenite Grain 3	20.04	7.01	2.19
Ferrite Grain 1	23.79	4.31	3.68
Ferrite Grain 2	23.61	4.36	3.73
Ferrite Grain 3	23.81	4.32	3.63

F—In 25 % Cr DSS Base Metal [29]				
	Cr	**Ni**	**Mo**	**N**
Austenite	23.5	8.2	3.5	0.48
Ferrite	26.5	5.8	4.5	0.06

6 Material Specifications

6.1 Typical Specification Requirements for Wrought Materials

Most users of DSSs in the petroleum industry have found that to ensure adequate corrosion and cracking resistance in service, special requirements need to be added to the purchase order for both the material and fabrication. The special material requirements are discussed in this section, while the fabrication requirements are provided in Section 7. The material requirements are added to the applicable ASME/ASTM specifications listed in Table 2. Annex A is an example of a specification containing the typical added material requirements for wrought products.

A nitrogen content of 0.14 %, minimum, in base metals of 22 % Cr DSSs is required in most refining services to ensure adequate corrosion and environmental cracking resistance at welds. Therefore, if UNS S31803, which has a specified nitrogen range of 0.08 % to 0.20 % is being used, it needs to be restricted to 0.14 % to 0.2 % nitrogen. UNS S32205 meets the required nitrogen range, as shown in Table 1, but presently is not in the ASME Code in all wrought product forms. It is believed that this situation will be remedied with time, as S32205 is being added to each wrought product specification as they are revised.

A water quench after final anneal is another common requirement specified to ensure the desired corrosion resistance. This minimizes the time the DSS is in the 982 °C to 705 °C (1800 °F to 1300 °F) range. One exception is that ASTM A480 permits air cooling of sheet and tubing when the sheet is processed in a continuous anneal and pickle line, but this is acceptable, as this method of cooling is very fast on thin sheets. For plates of even moderate thicknesses, simple air cooling will not yield the optimal condition. Rapid cooling is necessary to minimize the intermetallic phase content of the base material, particularly for material that is to be subsequently welded. The effect of time in the temperature range for the formation of intermetallic phases is cumulative, and quenching will help to reserve this time for welding and to ensure that the starting condition of the base metal will be uniform and consistent.

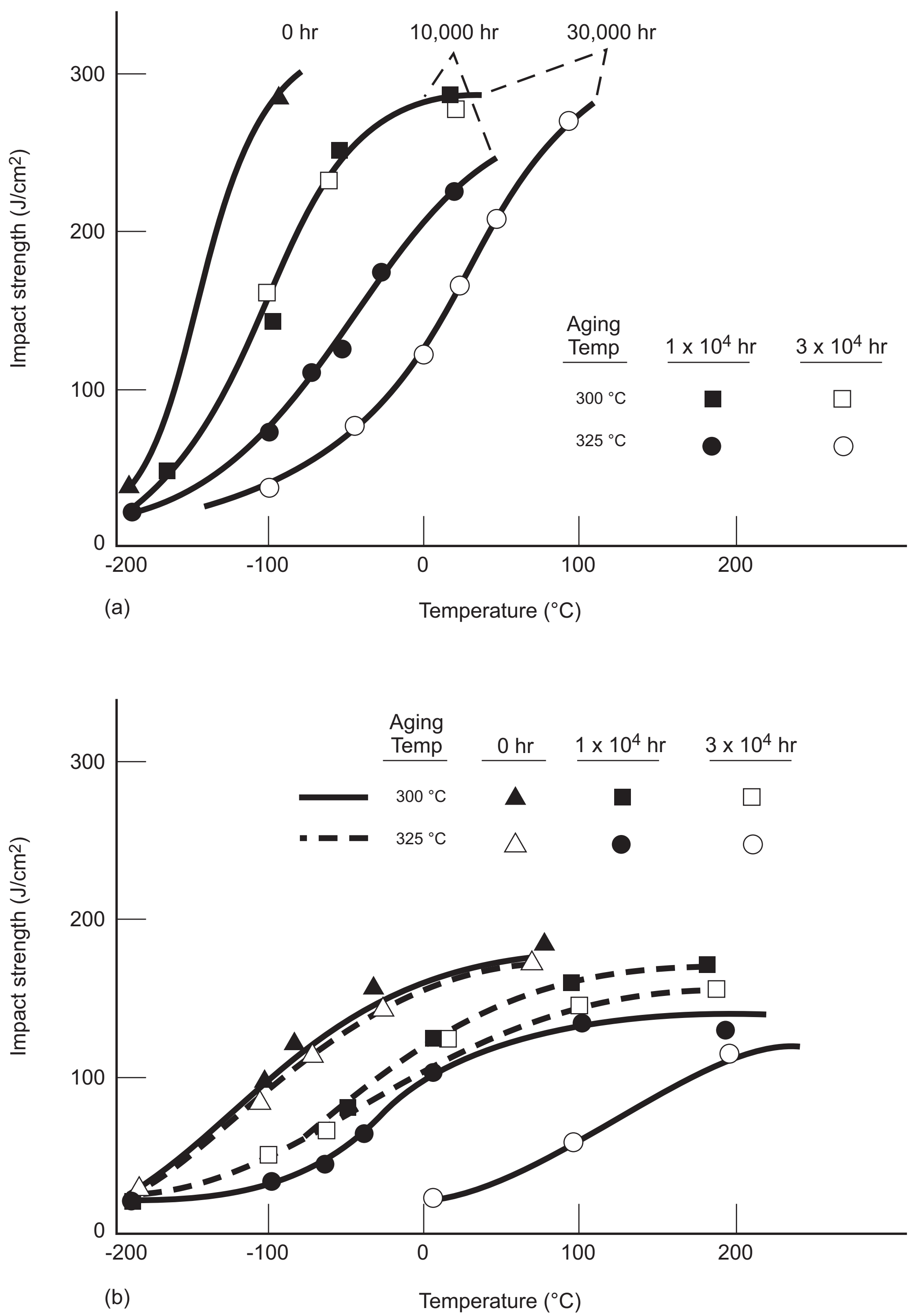
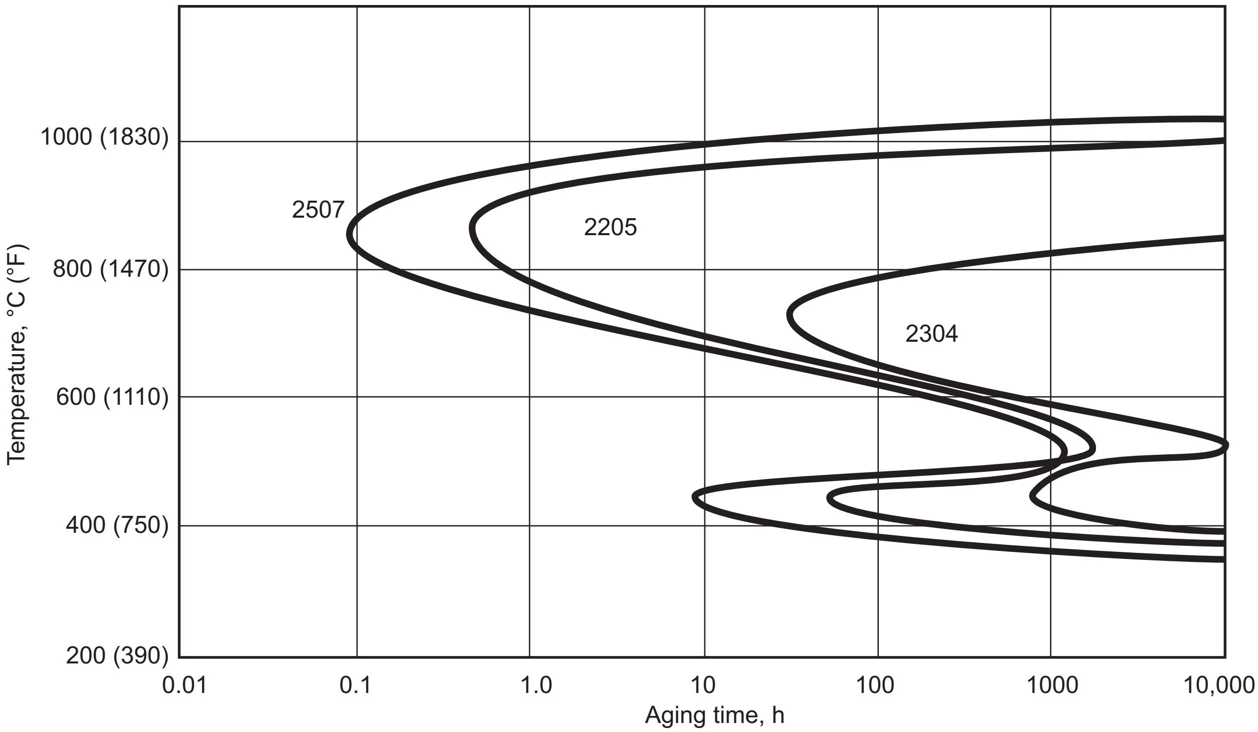


Figure 10—Impact Energy Curves for Alloys Aged at 300 °C and 325 °C:
a) Quench Annealed S32750; b) 45 % Cold Worked S31803 [2] [°C = (°F – 32)/1.8]



NOTE To the left of the curves, the impact strength is 27 J (20 ft-lb) or more.

Figure 11—Embrittlement of UNS S32304, S32205, and S32507 after Long Time Annealing [30]

To avoid possible detrimental effects of intermetallic precipitates, most refiners' purchase specifications call for a test to indicate their content. If intermetallic precipitates are present, they will affect both low-temperature toughness and corrosion resistance in most aqueous services. The tests typically used for Standard and Super DSS grades are ASTM A923 Test Method B, Charpy V-Notch toughness testing, and/or Test Method C, ferric chloride corrosion testing. The toughness test is done not to show adequate toughness for service (although this is also achieved and generally meets requirements for toughness testing per Code as long as the lateral expansion is reported), but rather to show the presence or absence of intermetallic precipitates, which affect both toughness at –40 °C (–40 °F) and the corrosion resistance in most aqueous services.

The acceptance criteria for the various DSSs base metals, weld metals and heat affected zones given in ASTM A923 were selected because they reliably correlate with the presence of intermetallic phases. For 25 % Cr alloy UNS S32750, ASTM A923 states that "the minimum impact energy shall be agreed upon by seller and purchaser." Some limits which are typically used for base metals and HAZs are: test at –46 °C (–50 °F), and meet 70 J average, 65 J minimum (52 ft-lb average, 48 ft-lb minimum).

For Test Method C, acceptance criteria are provided in ASTM A923 for S31803 and S32205 base metal and weld metal, and S32750, S32550, and S32520 base metal. It is expected that other grades will be added, but until then the test method can be applied to other grades, subject to agreement on the test temperature and acceptance criterion.

Tubing of Standard and Super DSS grades is treated differently as far as testing to ensure optimum corrosion resistance. ASTM A923 Test Method A is typically used. This test involves examining the metallographic structure for evidence of intermetallic phases after etching that brings out the intermetallic phases and the ferrite sequentially. Once the ferrite is stained dark without the indications of the intermetallic phases, as shown in the ASTM A923 acceptance figures, it is then concluded that the intermetallic phases are absent. ASTM A923 Test Method C can also be required for tubing.

27 %Cr Hyper DSS tubing is typically specified to pass an ASTM A923 Method C test, with a 24 hour exposure in a 6 % $FeCl_3$ solution at 80 °C (176 °F) and a criteria of weight loss of no more than 10 mdd.

Testing to measure intermetallic precipitates and to ensure proper corrosion resistance of Lean DSS grades is covered in ASTM A1084. It has tests which “parallel” the ASTM A923 tests, but are modified to be at test conditions which are appropriate for Lean DSS [31]. So far, the specification covers base metal grades UNS S32101 and S32304, and it currently does not address weld metals. One paper showed data from applying these tests to welds made on lean duplex SS with various filler metals [32].

Positive Materials Identification (PMI) testing is also specified by most purchasers to be done on all alloy pressure-containing base metal components and welds. It is a non-destructive test, and various details are given in API 578. This test helps ensure that the specified alloy grades are installed and avoids failures due to “mix-ups”.

6.2 Welded Versus Seamless Tubing and Piping

Many users allow either seamless or longitudinally welded tubing and piping. If GTAW, Plasma Arc Welded (PAW) or Laser welded tubing is allowed, some users require additional testing to verify the seamweld is free of defects, properly solution annealed followed by rapid cooling, and free of detrimental phases. For the seamweld, corrosion testing in accordance with ASTM A923 Method C for DSS and SDSS, or ASTM A 1084 Method C for LDSS, is typically required. For welded tubing which will be rolled into tubesheets, seamweld bead working or tube redrawing are often recommended to avoid excessive weld root penetration, which could be a risk during rolling. For nondestructive testing:

1) an electric test (eddy current); and

2) a hydrotest or air underwater test are typically required.

Welded piping is either made with filler metal (ASTM A928) with options regarding annealing to be specified in the order, or without filler metal (ASTM A790) with the pipe to be fully annealed and quenched after welding. In some cases, the filler metal is an overmatching DSS, and in others, it is matching. If weld filler metals are used, the optimum annealing temperature range may be tighter (and on the high side) than it is for the base metals.

6.3 Use of Integrally Finned Tubing

Integrally finning introduces high degree of cold work. For seam welded tubing, the bead working and annealing, prior to finning, needs to be optimized, especially for alloy 2205, which shows a higher degree of work hardening than lean duplex stainless steels. Experience has shown that if these production steps are not optimized, small cracks can develop in the seamweld fusion zone at the tube ID. Some users have required that a metallographic cross section be taken from the integrally finned welded tubing seam weld to verify a properly annealed microstructure and freedom of cracks at tube ID at the weldment.

One refiner reported extensive use of integrally finned duplex 2205 SS tubing in cooling water services. The tubes were longitudinally-welded and tests by the tubing supplier showed a significant hardness increase from the finning process, as expected based on the degree of cold working. Test results showed:

Bare tube before finning ....Rc 30

Fin valley..................................Rc 44

Middle of fin.............................Rc 39

Midsection of tube wall ....Rc 32

ID of tube wall ....Rc 36

Since some of the these cooling water bundles were in relatively severe services, such as wet sour services, chlorides, ammonium bisulfide (with or without cyanides), etc., this refiner conducted various testing in these environments to analyze the susceptibility to possible cracking. Some of the test results were:

Test	As-received Unfinned Tube	Finned Tube	Desired Limit
ASTM A923 Method C at 22 °C (mdd)	0.1, 0.1	0.1, 0.3	<10
ASTM G48 Method A at 30 °C (mdd)	37.9, 32.2 (with pitting)	40.2, 36.1 (with pitting)	<10
ASTM G48 Method A at 25 °C (mdd)	1.2 (no pitting)	1.4 (no pitting)	<10
ASTM G38 C-ring in 2 wt% NH4HS with 250 ppm chlorides (after 1 and 2 weeks; weld at peak of C-rings):			
1. C-Ring as tested:			
— With cyanides	No cracks	No cracks	No cracks
— Without cyanides	No cracks	No cracks	
2. C-Ring compressed:			
— With cyanides	No cracks	No cracks	
— Without cyanides	No cracks	No cracks	

These results showed that the finning did not affect the tests results, as the finned tube sections matched the bare tube test specimens. The unacceptably high ASTM G48-A test results at 30 °C were as-expected, as shown by data in 5.1.

6.4 Use of Twisted Tubes

Use of duplex 2205 SS twisted tubes has also been reported by various refiners. One case was cited in 5.3 of this report. It was installed in 1996 in a distillation column overhead service and failed by chloride SCC within two years. This refiner reported that replacement bundles of twisted duplex SS tubes which were solution annealed after twisting have been successful in preventing SCC. This seems to indicate that the residual tensile stresses from the twisting process are above thresholds for various SCC mechanisms, and hence for these services, the stresses should be relieved by a subsequent heat treatment (see also 7.3). Another interesting fact about this case history was that the u-bends were welded to the twisted tube sections.

In another case where 2205 twisted tubes were used in crude unit overhead service, the tubes failed by underdeposit chloride pitting in 18 months (which may have been unrelated to the "twisting"), and were replaced by twisted tubes of Hyper DSS grade S32707 [33]. Before these tubes were installed, ASTM G48 Method A tests were done at 80 °C, along with hardness and ASTM A923 Method A tests. The results were:

UNS S32707 Sample: (probably solution annealed)	Avg. Hardness on ID (HRC)	Avg. Hardness on OD (HRC)
Straight Tube Section	27.2	26.3
Twisted Tube Section	28.4	28.9

UNS S32707 Twisted Tube	Ferrite Content (%)	ASTM G48-A Test at 80 °C (mdd)
Samples A, B	40.3 ±1.2 %, 42.3 ±1.8 %	3.1, 2.6
Desired Limit	35 to 65 %	<10

Other services where duplex 2205 SS twisted tubes have been used include a distillate hydrotreater hot separator vapor trim cooler and a diesel rundown cooler. These exchangers used welded tube-to-tubesheet joints.

6.5 Duplex SS Castings and HIP Components

Annex D covers typical requirements for DSS castings for items, such as valve bodies and pump cases, in critical services. Annex D does not cover centrifugally cast line pipe. Annex E covers typical requirements for DSS HIP components. Some test results showing typical properties of HIP components and applications in the oil and gas production industry (including subsea) are given in the references [34], [35].

6.6 Duplex SS Used as a Cladding Material

Duplex SS has been used extensively as an explosion-cladding material on carbon steel for applications which do not require subsequent forming or heat treatment, as the duplex cladding would be degraded by any heat treatments required on the carbon steel after forming or welding. The most common application is for thick tubesheets and cladding layers of 8 mm to 19 mm thickness have been used. These applications have included both Standard and Super DSS grades and have been for numerous different industries.

The full range of DSS cladding thickness applied by the explosion-cladding process has been about 3 mm to 19 mm to date and there are also cases of titanium cladding being explosively applied to DSS base metal with thicknesses of 25 mm to 152 mm.

7 Fabrication Requirements

7.1 Typical Specification Requirements

In addition to special requirements on the materials, special welding and fabrication requirements are also needed to ensure proper corrosion and environmental cracking resistance. These requirements are not difficult, they are just “different” compared to austenitic SSs. Hence, with proper awareness, training and quality control, successful welds can be achieved. These restrictions are applied in addition to the applicable Code requirements.

The goal of these additional restrictions is to ensure that the fabrication procedures will not significantly diminish the corrosion resistance, mechanical strength or toughness of the steel. Typical specifications add requirements on the topics listed in 7.1.1, 7.1.2, 7.1.3, and 7.1.4.

This document previously included examples of specifications for Duplex SS weld procedure qualifications in Annex B and special production welding requirements in Annex C. These Annexes have been deleted in the Third Edition of this document, as recent revisions to API 582 address these requirements.

7.1.1 Welding Procedure Qualification (WPS/PQR)

The following are typical specification requirements for WPS/PQR (in addition to applicable Code requirements).

a) Added essential variables for each process;

b) The following additional tests—listing the test methods, sample number and locations, and criteria:

   1) ASTM A923 or A1084 (as applicable): Test Method B and/or Test Method C for standard and lean DSSs; and both tests for 25 % Cr and higher alloys with criteria to be agreed to by purchaser,

   2) Microstructure: measurement of intermetallics and percent ferrite from point count (see 7.4),

   3) hardness survey; and

c) Qualification of critical repair welds with a partial penetration joint detail (and consideration of cumulative heat implications).

7.1.2 Welding

The following are typical specification requirements for welding (in addition to applicable Code requirements):

a) cutting and joint preparation restrictions;

b) welding process restrictions;

c) a list of acceptable filler metals (including permissible over-alloyed and nickel-based filler metals);

d) the maximum and minimum heat input;

e) a maximum interpass temperature;

f) GTAW root passes for single-sided welds with filler addition and cold-pass technique (thin gauge material [less than about 3 mm] can be welded without filler metal);

g) the backing and shielding gas compositions;

h) heat tint removal on the process side, when accessible;

i) removal of arc strikes (arc strikes should be on the previous run [preferably] or in the joint).

7.1.3 Tube-to-tubesheet Joints

The following are typical specification requirements for tube-to-tubesheet joints:

a) some users: prohibition of rolled joints, except light rolling (<2 %) for positioning (due to possible high hardness) and requirement of strength welds with filler metal;

b) other users: allowance of rolled joints or rolled and welded joints with prequalification mockup tests, including hardness testing;

c) if welding, requirement of mockup and other tests as part of WPS/PQR.

7.1.4 NDE of Production Welds

The following are typical specification requirements for NDE of production welds (in addition to applicable Code requirements):

a) PT of backgouging;

b) PT of completed welds;

c) percent ferrite measurement, with feritscope and calibration to AWS A4.2;

d) code-required NDE with added RT of high pressure and other critical welds.

7.2 Typical Welding Processes and Filler Metals

The acceptable welding processes include GTAW, SAW, GMAW, SMAW and FCAW (see 4.4). Commonly used filler metals are shown in Table 9. Even though the weld filler metals used for welding of standard duplex SS grade 2205 has higher nominal nickel content (9 %) than the base metal (5 % nominal), they are often referred to as “matching”.

Table 9—Welding Consumables

Process	22 % Cr	25 % Cr (Note 1)	27 % Cr
SMAW	SFA 5.4 E2209	SFA 5.4 E2553, E2594, or E2595	Not applicable
GTAW/GMAW	SFA 5.9 ER2209	SFA 5.9 ER2553, or ER2594	As recommended by alloy supplier
SAW	SFA 5.9 ER2209 with a flux designed for DSSs	SFA 5.9 ER2594 with a flux designed for DSSs	As recommended by alloy supplier
FCAW	SFA 5.22 E2209TX-X or EC2209	SFA 5.22 E2553TX-X, E2594TX-X, EC2553, or EC2594	Not applicable
NOTE This table does not cover some of the specialized 25 % Cr alloys. The material manufacturer's (i.e. the alloy supplier's) recommendations on welding consumables should be followed.			

7.3 Dissimilar Metal Welding

For dissimilar metal welding, it is generally possible to weld DSSs to carbon steel, alloy steels, austenitic SS, and other grades of DSSs (although PWHT requirements need to be considered). The important points to note in selecting the filler metal are to obtain a weld metal with strength and corrosion resistance superior to at least one of the dissimilar metals, and to achieve a phase balance that will ensure a mechanically tough weld. A duplex filler metal is generally used for welded joints between DSSs and CS or austenitic SS, but austenitic SS filler metals have also given satisfactory results. Examples of these DSSs filler metals are indicated for 22 % Cr and 25 % Cr DSSs in Table 9. Manufacturer's recommendations are typically followed when welding DSSs to other alloys, along with the recommendations in API 582.

When welding DSSs to carbon or alloy steels, consideration is usually given to the potential detrimental effects on the DSS of the preheating or PWHTs required by the carbon or alloy steel. Preheating may slow the cooling of the DSS HAZ enough that intermetallic phases form. Most PWHTs for steel will lead to formation of intermetallic phases in DSSs. It may not always be possible to weld DSS to carbon or alloy steel and have both sides of the weld in an optimal metallurgical condition. One solution is to butter the CS or low alloy with austenitic filler metal (e.g. E309L), PWHT and then weld to the DSS using a DSS filler metal.

In some cases, Ni-based filler metals are proposed for either dissimilar metal welds or duplex welds. However, Ni-based fillers may give rise to a fully ferritic zone adjacent to the fusion line in DSS, which would not meet the desired ferrite requirement. This zone tends to give reduced toughness of the weldment. There can also be intermetallic phases formed in the weld metal, resulting in reduced corrosion resistance. Nickel-based filler metals containing niobium (Nb) have reportedly resulted in low weld metal toughness and solidification cracking and should be avoided, but other high Cr, high Mo nickel-based filler metals (with <0.5 Nb) have been used successfully, such as ENiCrMo-4, ENiCrMo-10, ENiCrMo-13, and ENiCrMo-14.

7.4 Ferrite Measurements vs. Austenite Spacing

Achieving the proper phase balance in weld deposits and heat affected zones is a critical concern during welding and is verified by ferrite measurements done on the weld procedure qualification samples. Although ferrite measurements in various areas of the microstructure using the ASTM E564 point count method are difficult and the accuracy between laboratories has been poor, no better test has yet been devised. Another test method measures "austenite spacing" and is referenced within one other industry standard for thick wall components (>25 mm). However, the results of a test program using this method were recently presented at NACE and this testing showed that the austenite spacing test is not valid for verifying the proper phase balance [36].

When obtaining ferrite measurements with the ASTM E564 manual point count testing method, an experienced laboratory should be used. One expert reported that doing an electrolytic etch in 10 % oxalic, prior to the NaOH or

KOH etch, results in the phases standing out better (oxalic clearly shows the phase boundaries and any nitrides, which will not show with caustic etching alone).

The automatic image analysis techniques in ASTM E1245 are not yet developed with the necessary procedure details for the purpose of determining the ferrite content in DSS wrought materials and weldments.

7.5 Cold Working and Hot and Cold Bending

Solution annealing is generally required by Code or purchaser specifications after cold work exceeds 10 % deformation for 22 % Cr DSSs and on all cold worked or bent (hot or cold) components of 25 % Cr DSSs (except on heat exchanger U-bends). If the cold deformation will exceed 15 %, an intermediate anneal may also be required. This applies to tube and pipe cold bending and other cold forming operations. Except for the issues regarding avoidance of SSC, higher limits might reasonably be considered if the fabrication equipment is capable of dealing with high-strength DSSs.

Heat exchanger U-bends are difficult to heat treat without some zone of the tubes being exposed to an unacceptable temperatures, which results in impaired corrosion resistance. With furnace heat treatments, which typically only have the bends inserted into the furnace, the tangent lengths can be exposed to an unacceptable temperature. In addition, testing has shown that the properties of the U-bends without heat treatment are acceptable for refinery services down to bend radiuses of 1.5 times the tube diameter for super DSSs grades and at least 3.3 times the tube diameter for S32205. Hence, various users have concluded that no heat treatment of U-bends should be specified, as long as there is a 3.3D minimum radius for 2205 DSS (the inner row of tubes can be installed with the U-bend diagonal and with a few less tubes to accommodate this larger minimum radius) [37].

In the cases where heat treatment of U-bends is specified, resistance or capacitance heating has been used successfully with procedures carefully designed to minimize the time of tube exposure to the 700 °C to 950 °C (1300 °F to 1750 °F) range.

Hot bending of piping is generally done using the induction bending process and the procedures are qualified with test bends and various essential variables. The bending temperature for 22 % Cr is typically in the range of 1000 °C to 1066 °C (1830 °F to 1950 °F). During induction bending, DSS pipe is purged with nitrogen or argon (0.5 % maximum oxygen). Bends produced from 22 % Cr DSS are solution annealed, if needed, to meet the required mechanical properties. After final heat treatment of any DSS bend, a chemical descaling and neutralization treatment is typically done. Any longitudinal welds normally receive 100 % RT after bending and the bend surface typically receives 100 % PT. Dimensional and hardness testing are also performed.

7.6 Tube-to-tubesheet Joints

Tube-to-tubesheet welded joints can be prone to high hardness due to rapid cooling and tube-to-tubesheet rolled joints can be prone to high hardness due to the cold work. This is a concern since many DSS heat exchangers and air coolers used in refining are primarily in relatively severe wet sour services where high hardness (approximately >320 HV for LDSS or DSS and >350 HV for SDSS) would be unacceptable. For shell-and-tube exchangers, the preferred type of tube-to-tubesheet joint is determined on a case-by-case basis. Strength welding with light rolling only (<2 %) has been used for wet sour services, or a rolling procedure that results in acceptable hardness for the specific material grade and exchanger design have been used. To test the tube-to-tubesheet joint acceptability, whether it is welded, rolled or welded and rolled, a mock-up is often required to prequalify the procedure.

Over-alloying of these welds (which are generally made with the GTAW process), such as with ER2509 or Ni-based (Nb free) filler metal, can also be considered in order to help provide a better HAZ phase balance, even with the inherent low heat input. Another option for alloy 2205 DSS tube-to-tubesheet joints is to use alloy 309Mo or 309LMo SS GTAW filler metal with argon-2 % nitrogen shielding gas when an austenitic weld is acceptable for the service. The nitrogen in the gas and the higher nickel content in the filler metal give a better phase balance in the HAZs of these low heat input joints. Some users require argon-2 % nitrogen shielding gas for matching filler metals also.

When rolled joints are used, seamweld tubing root penetration needs to be considered. Some users specify beadworking for seamwelded DSS tubing, as discussed in 6.2. Rolled joints for less severe services (e.g. most cooling water and non-wet sour hydrocarbons) can be used with less precaution to minimize the risk of high hardnesses. Also, one test program with various degrees of rolling and rolled joints, with and without welding, did not show any of the rolls to have unacceptably high hardnesses [38].

In some severe services removal of the crevice to prevent corrosion from the shell-side service may be needed. When the shell-side service is seawater, some exchangers have been fabricated with crevice-free backface welding techniques that involve seal welding of the tubes on the backside of the tubesheet.

For the mock-up used to prequalify the tube-to-tubesheet welding and/or rolling procedures, ASME Section IX, QW-193 is generally followed with additional special requirements. The assembly of the mock-up is typically required to simulate all steps of the production joint, including both welding and rolling. In addition, if production welding is to be performed through the plug sheet, this should be simulated in the test assembly. Past testing has specified that the access hole diameter and distance from hole to tubesheet shall be equal to production distances ±10 %. For testing, in addition to the macro-examination required by ASME Section IX, QW-193, the microstructure, microhardnesses and ferrite contents of one randomly selected weld section is typically analyzed (both in the weld and HAZs). In some cases, for standard and SDSS grades, a quadrant section of a tube-to-tubesheet weld may also be subject to corrosion testing with no pitting allowed.

7.7 Post-Fabrication Cleaning

The main objectives of post-fabrication cleaning are to:

— remove significant welding heat tints;

— remove weld spatter, flux, slag or arc strikes;

— remove surface contamination from smeared or embedded iron;

— remove surface contamination from dirt, oil, paint or crayon marks;

— ensure there is an adherent, continuous, protective, chromium-rich oxide layer on the entire surface.

Weld spatter, flux, slag, arc strikes, and some weld heat tints can be removed by mechanical cleaning, such as fine abrasive grinding or with a stainless steel wire wheel or brush. A “fine” grinding wheel is typically used, as coarse grinding marks can be another source of disruption of the protective passive oxide layer by allowing deposits to stick to the surface. For removal of heat tints and other contaminants the order of efficiency of the cleaning methods is:

— blasting,

— grinding,

— pickling and passivation,

— electropolishing.

The best corrosion resistance is obtained by mechanical cleaning followed by chemical pickling and passivation [39].

7.8 NDE Methods

For Code-required NDE of welds, RT is relatively straightforward for DSSs and standard techniques can be used. However, UT requires specialized techniques due to the anisotropic nature and relatively large grains of DSS welds [2].

7.9 Hydrostatic Testing

Some specifications limit the chloride content of hydrotest water to 50 ppm, similar to austenitic SSs, to minimize the risk of chloride pitting or SCC during startup. However, other users consider that with the demonstrated resistance of UNS S32205 to much higher levels of chloride and higher temperatures in long-term service, this limit is unnecessarily conservative and costly. In any case, particular attention should also be given to drying of the equipment after hydrostatic testing in order to minimize the risk of microbiologically influenced corrosion (MIC).

7.10 Coating Requirements and Risk of CUI

Duplex SS components which are insulated and in an area where the climate or atmospheric conditions and the operating temperature range create a risk of external corrosion or chloride SCC due to CUI (see 5.1 of this report), are typically externally protected in a similar manner as austenitic SS. NACE SP0198 addresses this concern and gives recommended protection systems. Non-insulated DSSs are typically not coated as they have excellent atmospheric corrosion resistance.

8 Examples of DSSs Applications within Refineries

Numerous data sources were reviewed to compile a list of past uses of DSSs within refineries. One source that provided many case histories was NACE International's Refin-Cor database. Refin-Cor is a compilation of approximately 50 years of meeting minutes from the Refining Industry Corrosion Group. Table 10 shows the results of a search within this database. The item number is the paragraph identifier within the minutes and the first two digits indicate the year the item was presented. Table 11 shows other case histories from various published and unpublished sources, such as DSS material suppliers' case history reports and published literature primarily from users.

A list of the applications and the corresponding corrosion or other failure mechanisms that led to the selection of DSS is shown in Table 12. However, users are cautioned that in some services standard duplex grades may be inadequate and higher DSS grades are preferred. Failures have occurred under some conditions, as listed in Table 10. Also, failures can occur in almost all services if DSS is of poor material quality or is improperly fabricated.

Table 10—Case Histories of DSS Uses Reported in NACE International Refin-Cor

Item No.	Unit	Service	Grade	Problems	Comments
02F5.19-36	Amine	MEA Reclaimer	2205	None	Replaced 300 series SS which suffered Cl SCC
08C4.24-11	Amine	MEA Reclaimer	2205	Pitting in ends of U-bends (150 mm lengths) due to improper heat treatment. Remainder of tube "working very well".	No longer using heat treatment of DSSs U-bends
97F5.4-01	Coker	Fractionator overhead condenser	2205	Isolated pitting on process side after four years	Both base metal and weld. On ferrite not austenite
03C5.4-01	Coker	Fractionator overhead condensers	2205	None	Replaced 70-30 Cu-Ni which had a six-year life and failed by corrosion and/or denickelification. Costs were the same
90F9.16-40	Cooling Water	>250 °F on process side	2205	None	Examples: FCC fractionator overhead and vacuum overhead condenser
02F5.17-01	Cooling Water	Fresh water recirculated CW exchangers at three refineries	2205	None. Have not found practical material for floating heads yet (using coated CS or 316 SS to date).	Welded DSSs tubes was found to be cost comparable to brass and readily available
08C4.16-10	Cooling Water	Critical bundles in fresh water CW service	2205	None	Replacing CS bundles that were not lasting for two runs
08C4.16-17	Cooling Water	Numerous bundles in fresh water CW service	2205	None	Recently did internal survey; no signs of MIC; good service; replace CS tubes (reusing CS tubesheets) regularly; cost is about twice compared to using CS tubes
80C5.2-04	Crude	Overhead condenser and desalter effluent exchanger	3RE60	One manufacturing problem	
80C5.2-05	Crude	Desalter effluent exchanger and top P/A exchanger	3RE60	OK in desalter effluent; failed faster than CS in top P/A due to hot chloride pitting	
80C5.2-06	Crude	Overhead	3RE60	None	Test tube; showed 2 mpy to 3 mpy
87F7.1-13	Crude	Overhead condenser	3RE60	Failed by SSC in a few months	Test tubes
89C7.2-09	Crude	Tower top lining	2205	None	Previous sulfur corrosion of Monel due to increasing temperature to >250 °F
89F9.2-05 91C9.1-01	Crude	Vacuum overhead condenser	2205	None	Went to 2205 due to fouling problems on CS; not corrosion

Table 10—Case Histories of DSS Uses Reported in NACE International Refin-Cor (Continued)

Item No.	Unit	Service	Grade	Problems	Comments
92C5.1-16	Crude	Instrument tubing	2304	None	Replaced 316 SS that failed by SCC
97F5.1-06	Crude	Tower internals		SCC due to hot caustic	Also cracked 316 SS and corroded 410 SS
98F5.2-24 99C5.2-01	Crude	Fractionator overhead condenser	2205	Some pitting and fatigue	(Later replaced due to wear at enlarged baffle holes)
00F5.2-34	Crude	Tower packing in top pump-around area	DSSs	None	Replaced Monel, which corroded due to evaporating sour water and deposited salts
01F5.2-45	Crude	Fractionator overhead condenser	2205/2507	2205 corroded and was replaced with 2507. Shock condensation	Replaced ferritic SS which eventually corroded
01F5.2-46	Crude	Fractionator tower cladding in top section	2205	Did well—minor pitting which did not affect serviceability	CS had corroded through
98C5.2-10	Crude/Bitumen	Fractionator overhead condenser	2205 twisted tube	None	OK after one year. Fouling service
77F6.3-01	FCC Light Ends	Slurry/splitter feed	3RE60	None	Test tubes
98F5.5-02	FCCU	Light ends reboiler		None	Stress relieved U-bends, pickled. They believe pickling provides a good passive film
98F5.5-04	FCCU	Diluent recovery unit	2205 twisted tube	Failed due to CSCC at residual stress patterns in the tubes (from both sides?)	Overhead is acidic due to Cl and neutralized with ammonia. Also CW has significant Cl
85C9.2-01	H_2SO_4 Alky	DIB overhead condenser	3RE60	Failed due to fluoride deposits (10 % to 15 % F)	Fluorides in purchased feedstocks. Went to Sanicro 28
10C4.19-01	Flare Gas Recovery Unit	Coker flare gas recovery liquid ring compressor impeller	Cast duplex SS	None	Previous cast 316 SS impeller failed by chloride SCC. They have numerous flare gas recovery liquid ring compressors made of DSS.
98F5.8-01	HDS	REAC	3RE60	CSCC under deposits	At 300 °F to 400 °F where deposits collected
98F5.8-02	HDS	Exchanger	2205	SCC under NH_4Cl deposits	Rest of exchanger was in pristine condition
97C5.8-08	HDS	Stripper overhead air cooler	2205	None	Survey—also piping and cladding in tower top
89C7.6-06 96C5.10-09	HDS	REAC	3RE60	Extensive header weld cracks from fabrication	Used CS as a temporary replacement
91C9.7-01	HDS	Stripper fractionator tower top cladding	2205	None	Previous NH_4HS/NH_4Cl corrosion on 309 overlaid CS in one year. At 250 °F to 280 °F

Table 10—Case Histories of DSS Uses Reported in NACE International Refin-Cor (Continued)

Item No.	Unit	Service	Grade	Problems	Comments
96C5.10-03	HDS	REAC	2205	None—recently installed	8 % NH_4HS; 25 fps to 30 fps
96C5.10-06	HDS	REAC	2205	None	OK after four years. At Husky Oil. 4.9 % NH_4HS
96C5.10-07	HDS	REAC			Referred to Corrosion/97 paper which includes successes and failures
96C5.10-08	HDS	REAC			Production paper discusses hydrogen uptake from galvanic couple
96C5.10-11	HDS	Last effluent exchangers	3RE60	None	OK after 17 years. Another bundle in hotter service failed by 885 °F embrittlement (operating temperature ≥600 °F)
00F5.8-12	HDS	REAC outlet piping	2205	None	Replaced corroded CS. NH_4HS is 8 % to 10 %, with 18 fps to 20 fps and water wash
04F5.7-31	HDS	REAC	2205	None. 2205 tubes in CS header boxes. Also in cat feed HDS and hydrocracker	Tubes were seal welded to header box. In one case, the CS header suffered nozzle corrosion due to NH_4HS
86F7.3-02	HDS—Cat Feed	Feed/effluent (?)	3RE60	Good	CSCC of austenitic SS. Test tubes
73F8.4-01	Hydrogen Plant	MEA reboiler	3RE60	None	Previous SCC of 304 SS with 1000 ppm Cl
97C5.7-03	Hydrogen Plant	Pot. carbonate CO_2 removal reboiler	2507	None	OK after 5 years. Replaced corroded CS. Used welded tube to TS joints
86F7.3-03	Hydrocracker	Reactor effluent/stripper feed	3RE60	Cracked by SCC in four months from stripper feed side	Mechanism not defined. Concerned with high H_2S and chlorides
87F7.3-04	Hydrocracker	Fractionator feed/reactor effluent	2304	None.	Replaced 304SS, which failed in four years due to CSCC from reactor effluent
94C5.8-01	Hydrocracker	Feed/effluent exchangers (2nd stage)	3RE60	Failed—CSCC from OD and hydrogen cracking from ID	
96C5.9-06	Hydrocracker	CW at 150 °F	2205	None	OK after two years. Replaced SS that failed by SCC at a U-bend
85C14.8-03	Pipeline	Containing wet CO_2	2205	None	17 miles; cheaper than 316L
85C14.8-06	Pipeline				Under design; in Alaska; did an economic study

Table 10—Case Histories of DSS Uses Reported in NACE International Refin-Cor (Continued)

Item No.	Unit	Service	Grade	Problems	Comments
99F5.16-04	Steam Gen.	Steam generator with sour water on other side	2205	None	
79C9.1-04	SWS	Feed/bottoms	3RE60	None	API Survey result
79F9.1-01	SWS	Reboiler	3RE60	None	Test tubes
80F11.1-05	SWS	Reboiler	3RE60	Failed in less than a year	Gas plant
86C11.2-01	SWS	Stripper overhead	3RE60	Good after 18 months	Previous problems with CS, 304SS, Inconel 600 and Ti
86F7.10-02	SWS	Stripper overhead	3RE60	None	
88C7.10-03	SWS	Reboiler	2205	Failed by under-deposit pitting after three to four years	
88C7.10-04	SWS	Reboilers and feed/bottoms exchanger	3RE60	None	OK after 15 years
88C7.10-06	SWS	Overhead air cooler and feed/bottoms exchanger	3RE60	None	OK after three to four years
95C5.5-06	SWS	Stripper overhead	2205	None	
95C5.5-20	SWS	Stripper overhead	2205	None	
96F5.12-02	SWS	Reboiler	2205	None	Corrosion of CS. 316 also acceptable
05C5.11-01	SWS	Piping	2205	None	Replaced hydrided Ti
05C5.11-03	SWS	Overhead exchanger	2205	Failed after three months due to preferential attack of the austenitic phase	Replaced aluminum which failed after 18 months due to erosion

Table 11—Case Histories of DSSs Uses Reported by Other Sources

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
Amine	2205	—	0.13 mole % H_2S, 0.9 mole % H_2O	237/115	87	CW with 600 to 1000 Cl, chromates inhib.	86/91	90	Started service in 1983
Amine	2205	304 SS	Amine, CO_2, cyanide, NH_3, H_2S, polysulphides	—	—	Steam	—	—	Delivered in 1987. U-bends. CS failed. Note 1
Amine	2205	2205 (F51)	Heating medium	284/212	309	Rich MDEA, CO_2	160/165	196	CO_2 removal plant, rich amine heater, seven years good service to date. Tubes see 13.7 fps. Expanded and strength welded
Crude	2205	CS	APS overhead	312/240	11	Undesalted crude feed	121/240 - series	417	Two bundles. Only bottom half
Crude	2205	CS	Wet naphtha (OH)	240/110 (from A/C)	8	CW	—	—	Two bundles
Crude	2205	—	Wastewater—1000 ppm maximum Cl, 5000 ppm maximum H_2S, about 300 ppm NH_3	104/194	—	Desalter Eff. Water—6000 ppm maximum Cl	257/140	—	Installed in 1984
Crude	2205	—	Air	—	—	Desalting—15 % mole fract. CO_2, 2 ppm to 5 ppm HCl, 2 ppm H_2S	221	250	In service since 1982
Crude	2205	—	Steam	203/194	145	Crude oil	68/140	362	Four bundles—Installed in 1983
Crude	2507	2507	Naphtha pump-around, water, chloride salts	—	—	CW	—	—	The tubes had extensive CSCC on the OD after approximately one year
Coker	Dupl.	CS	Overhead compressor interstage	250[a]/105	37	CW	—	—	Two bundles. Channel coated with epoxy phenolic
Coker	Dupl.	CS	Overhead compressor after cooler	250/105 (Note 2)	145	CW	—	—	Two bundles. Channel coated with EP; Shell 304 SS clad
Distillation	2205	—	Gasoline with sulphur	A: 192/219 B: 205/255	—	Hydrocarbons, water, some chlorides	A: 302/219 B: 349/273	—	Ordered in 1984. CS lasted two years

Table 11—Case Histories of DSSs Uses Reported by Other Sources (Continued)

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
FCCU	2205	CS w/304L SS clad	Fractionator overhead	240[a]/100	5	CW	—	—	Eighteen bundles. Shell SS clad also on B, D, F
FCCU	2205	CS w/ Belzona	Cat gas	238/100	40	CW	—	—	Four bundles. 2205 installed in 6/98
FCCU	2205	—	Gas from FCC distillation	238/126	—	Treated water	68 to 99/ 201 to 220	—	Installed in 1988. CS lasted six years
Hydro-cracker	2205	—	Air	—	—	Gas with 6 % H_2O, 0.16 % NH_3, 77 % H_2, 3.1 H_2S	266/122	1740	In service since 1983
Hydrode-sulfurization	2205	—	BFW	221/390	—	Process gas	725/374		Ordered in 1985
Hydrode-sulfurization	2205	—	Gasoil, H_2O, NH_4HS (30 %)	285/340	285	Steam	645/570	320	Installed 1987. CS lasted three years
Hydrode-sulfurization (ARDS)	3RE60/ 2205	CS/ 2205	Air	—	—	HHPS Overhead, high NH_4HS	Not reported	Not reported	Orig. CS headers and 3RE60 tubes. CS nozzles. Outlet downcomers corroded leak/fire in five to six years. Replaced with 2205 in 1981. Tubes were 0.065 in. minimum. Now many are close to t_{min} of 0.050 in. (0.5 mpy to 0.7 mpy). Some tubes have been plugged.
Hydro-processing	2205	2205	Air	—	—	Reactor effluent	—	2300	SSC of multiple tube-to-tubesheet welds shortly after Jan. 2002 startup – some within 48 hours. Some welds confirmed to have high ferrite (see Reference 23).
Hydro-processing	2205	2205	Air	—	—	Reactor effluent; 3.8 wt.% NH_4HS in sep.	—	1200	Nov. 2003. Cracked pipe weld at REAC outlet; cracking within weld; weld hardness and ferrite were acceptable. 1.25 in. of pipe spring-back at failure location. 5 years of service (see Reference 23).

Table 11—Case Histories of DSSs Uses Reported by Other Sources (Continued)

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
Hydro-processing	2205	2205	Air	—	—	Reactor effluent; 6 wt.% NH_4HS in sep.	—	2000	Mar. 2005. 32 in. fracture in header box weld. Cracking along fusion line. Some high ferrite and high hardnesses found in weld and HAZs; 9 years old (see Ref. 23)
Hydro-processing	2205	2205	Air	—	—	Reactor effluent; 7 wt.% NH_4HS in sep.	—	2300	June 2006. Multiple REAC outlet header and outlet piping weld cracks; some cracks within welds and some along fusion lines; some high ferrite at welds IDs; 2 years (see Ref. 23)
Hydro-processing	2205	2205	Air	—	—	Reactor effluent; 6 wt.% NH_4HS in sep.	—	2050	Oct. 2009. Header box rupture during pressure test following repairs to cracked tube-to-tubesheet welds; cracking along fusion line. Weld ferrite and hardness all okay. 6 years of service (see Ref. 23)
Hydro-processing	2205	2205	Air	—	—	Reactor effluent; 6 wt.% NH_4HS in sep.	—	2475	Sep. 2010. Leak in pipe-to-nozzle weld at REAC outlet; found by Inspector about to inspect weld for cracking; leak along fusion line; some zones of high ferrite found; 14 years of service (see Ref. 23)
Hydro-processing	2205	2205	Air	—	—	Reactor effluent; 11.5 wt.% NH_4HS in sep.	—	1550	Mar. 2012. Multiple tube-to-tubesheet leaks during hydrotest after a turnaround heat exchanger cleaning and 8 years of service. New in 2004 and built with latest specifications (see Ref. 23)
Hydro-processing	2205	2205	Air	—	—	Reactor effluent; mostly ≤5 wt.% NH_4HS in sep.	—	From 250 to 2000	15 additional REAC recently inspected for possible cracking with no failures to date (see Ref. 23)
HCN Hydrofiner	2205	CS	Hot separator overhead	300/115	227	CW	—	—	Two bundles
HCN Hydrofiner	2205	CS	Hot separator overhead	115/105	221	CW	—	—	
HCN Hydrofiner	2205	CS	HCN product stripper overhead	196/115	85	CW	—	—	Two bundles

Table 11—Case Histories of DSSs Uses Reported by Other Sources (Continued)

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
Jet Hydrofiner	2205	CS	Jet fuel stripper overhead (also diesel stripper overhead from DHF – nnf)	323/100	110	CW	—	—	CW corrosion (A/C are CS; B/D are 2205 and in series)
Hydrotreating	2205	—	Reactor effluent	669/	—	Preheated effluent, <10 ppm Cl, H_2S	100/532	—	Delivered in 1983. CS corroded and 321 pitted
Hydrotreating	2205	—	Hydrocarbons	257/590	—	Effluent, 2 % to 3 % H_2S, NH_3	716/482	870	Installed in 1983. 321 failed by SCC
Hydrotreating	2507	—	Seawater	81/99	40	Hydrocarbons, 1.7 % H_2S, NH_3, 0.01 % H_2O	280/104	900	Delivered in 1989
SWS	2205	2205	Air	—	—	Stripper OH condenser, high NH_4HS, 60 ppm Cl, non-detectable CN	Not reported	Not reported	Failed after one year due to NH_4HS corrosion over 3 ft of the second pass. Replaced with 825 which also failed in one year. Now replacing with Hastelloy C
SWS	2205 Piping (sch. 10)	—	—	—	—	Stripper OH condenser, 15 to 22 % NH_4HS, 80 to 90 ppm CN	210	19	Initial failure after 4 years and additional failures after 7 years. Pitting in HAZs and away from welds. Properly fabricated. Corrosion due to high CN and NH_4HS.
Virgin Light Ends	2507	CS	Splitter overhead	111/100	205	CW	—	—	Sister bundle (A) is CS; CW corrosion

NOTE 1 In testing, 304 SS experienced pitting and stress corrosion cracking, while DSSs looked good.

NOTE 2 Inlet temperature is lower as there is a water injection.

Table 12—Summary List of DSSs Refinery Applications to Date

Application	Corrosion/Failure Mechanisms Resisted	Possible Failure Mechanisms [2]
Hydroprocessing units: Reactor effluent air coolers and piping Stripper overhead condensers and piping Stripper tower top cladding Fractionator feed/reactor effluent exchanger	 NH_4HS corrosion NH_4HS corrosion NH_4HS corrosion H_2/H_2S corrosion, CSCC	All applications: SSC Chloride pitting or CSCC under NH_4Cl deposits CN-accelerated NH_4HS corrosion
Sour water strippers: Reboilers Feed/bottoms exchangers Overhead condensers or pump-around exchangers	 Salt corrosion, CSCC NH_4HS corrosion NH_4HS corrosion	All applications: SSC Chloride pitting or CSCC under NH_4Cl deposits CN-accelerated NH_4HS corrosion
Crude units: Atmospheric tower overhead condenser and OH/ crude exchangers Vacuum jet condenser Atmospheric tower top cladding Desalter brine cooler Desalter feed/brine exchanger Exchangers with hot naphthenic streams on one side and streams containing aqueous chlorides (e.g. undesalted crude) on the other	 Salt corrosion, CSCC, wet H_2S, HCL corrosion Salt corrosion, CSCC, wet H_2S Salt corrosion, CSCC, wet H_2S Salt corrosion, CSCC Salt corrosion, CSCC Naphthenic acid corrosion and CSCC	All applications: SSC Chloride pitting or CSCC under NH_4Cl deposits
Amine units (H_2S removal): Regenerator overhead condenser Lean amine cooler Reboiler and reclaimer	 NH_4HS corrosion Hot amine corrosion Hot amine corrosion, acid gas corrosion, chlorides	All applications: SSC Chloride pitting or CSCC under NH_4Cl deposits CN-accelerated NH_4HS corrosion
FCC and light ends recovery: Fractionator overhead condenser Compressor intercooler Deethanizer reboiler	 NH_4HS corrosion NH_4HS corrosion Wet H_2S corrosion	All applications: SSC Chloride pitting or CSCC under NH_4Cl deposits CN-accelerated NH_4HS corrosion
Coker: Fractionator overhead condenser Fractionator overhead compressor intercooler and aftercooler	 NH_4HS corrosion NH_4HS corrosion	All applications: SSC Chloride pitting or CSCC under NH_4Cl deposits CN-accelerated NH_4HS corrosion
CO_2 removal plant (hydrogen manufacturing plant): Wet CO_2 pipeline Catacarb regen reboiler	 CO_2 corrosion CO_2 corrosion	
Brackish or salt water cooling water exchangers	Chloride pitting and SCC	Chloride pitting or CSCC under Cl salt deposits
Fresh water (recirculated and cycled) cooling water exchangers	Underdeposit corrosion	
HRSG boiler feed water heater coils	Oxygenated demineralized water and condensing flue gas	
Fuel gas piping	Condensed water with chlorides	
Instrument tubing (Note 1)	External CSCC	

NOTE 1 The high strength of DSS makes it difficult to bend in the field.

NOTE 2 These mechanisms can occur if the conditions are severe (i.e. over the limits for the given grade of DSS) and should be reviewed when selecting materials

Annex A
(informative)

Example of Special Material Requirements for DSSs

A.1 Plate, Pipe, Forgings, Fittings, Bar

A.1.1 Standard DSSs with approximately 22 % Cr shall be specified as UNS S32205 or as dual certified UNS S31803/S32205.

Super DSSs with approximately 25 % Cr shall be specified as UNS S32520, S32550, S32750, S32760, S32906, or equivalent. When specified by purchaser or the applicable materials specification, Super DSS 25 % Cr grades shall have a minimum PREN of 40.

Lean DSSs shall be specified as UNS S32304, S32101, S32003, S32202, S82011 or S82441.

Other specialized grades may be ordered by brand name when specified by purchaser.

A.1.2 Nitrogen for UNS S31803 shall be 0.14 % to 0.20 %.

A.1.3 Materials shall be water quenched and pickled after the final anneal by the materials supplier.

A.1.4 To ensure adequate corrosion resistance, each heat of material of Standard DSS grades (except for tubing and fasteners) shall be tested per Test Method B or Test Method C in ASTM A923, and meet the given criteria. The rapid screening test included in ASTM A923 shall not be used to accept material.

For Super DSS grades, both Test Method B and Test Method C shall be done. Test Method B for Super DSS grades, shall include testing at –46 °C (–50 °F), and shall meet 70 J average, 65 J minimum (52 ft-lb average, 48 ft-lb minimum). Test Method C for Super DSS grades shall include testing at 40 °C (104 °F) and shall meet 10 mdd maximum.

For Lean DSS grades, each heat of material (except for tubing) shall be tested per Test Method B or Test Method C in ASTM A1084, and meet the given criteria which shall be extended to all Lean DSS grades. The rapid screening test included in ASTM A1084 shall not be used to accept material.

For all grades, any impact testing required by the applicable design Code shall also be met.

A.1.5 Welded fittings (nozzles etc.) made from plate shall be 100 % RT examined at the fitting fabricators shop.

A.1.6 Swaged nozzles shall be heat treated in accordance with Table 1 of ASME SA-790 after the swaging operation.

A.1.7 Solution annealing is required after cold working on components (other than tubing) if the deformation exceeds 10 % for the lean or standard grades of DSS. All cold formed Super DSS (other than tubing) shall be solution annealed after cold forming.

A.1.8 Marking materials shall be suitable for SS and contain less than 200 ppm halogens and less than 200 ppm sulfur. When requested, composition certificates of marking materials shall be provided. Dye stamping of final products is prohibited.

A.1.9 Certified material test reports (CMTRs) are required for all materials.

A.2 Tubing

A.2.1 Tubing shall be seamless or welded tubing, and welded tubing shall receive both hydrostatic testing and nondestructive electric (eddy current) testing in accordance with ASME SA-789. Tubing shall be manufactured from steel produced by the electric furnace process and subsequent VOD or AOD. Secondary melting processes, such as VAR and ESR, are permitted.

A.2.2 Hyper DSS with approximately 27 % Cr, which is currently only available as tubing, shall be specified as UNS S32707. Hyper DSS shall always have PREN greater than 48.

A.2.3 Tubing shall be solution annealed in the temperature range listed for the particular grade in ASME SA-789 for sufficient time to eliminate intermetallic precipitates and then rapid cooled by water quenching, or air or inert gas cooling to below 315 °C (600 °F). Other heat treatments and quenching media other than water must be approved by purchaser. Welded DSS tubing shall be bead worked prior to in-line solution annealing followed by rapid cooling, unless otherwise approved by purchaser. Laser welded tubing can be annealed without prior bead working when approved by purchaser as long as it has proper root cleanliness and weld penetration.

A.2.4 The hardness testing criteria given in ASME SA-789 shall be modified to Rockwell C 28 maximum for lean and Standard 22 % Cr DSSs. Failure to meet this hardness requirement shall constitute failure of the specimen and shall result in hardness testing being required on each length in the heat lot represented by the specimen. For Super and Hyper DSSs alloys, the maximum hardness limits shall be in accordance with ASME SA 789.

A.2.5 For Standard and Super DSSs, ASTM A923 Test Method C shall be done and meet the required criteria, or if not given, then a criteria agreed to by purchaser and Supplier. 27 % Cr Hyper Duplex alloys shall pass a modified ASTM A923 Test Method C test, with testing for 24 hours in a 6 % $FeCl_3$ solution at 80 °C (176 °F) and have a weight loss of no more than 10 mdd. In addition for all these grades, one specimen representing each heat lot shall receive a microstructural examination per the requirements of ASTM A923 Test Method A. The presence of affected or centerline structures shall be grounds for rejection of the solution anneal batch represented by the specimen and the batch shall require reheat treatment and retesting. The sample size shall be a 2.54 cm (1 in.) long tube specimen for each heat lot.

A.2.6 For Lean DSSs, ASTM A1084 Test Method C shall be done and meet the required criteria.

A.2.7 No weld repairs to tubes are permitted.

A.2.8 Twisted tubes shall require solution annealing at the temperatures and cooling rates given in ASME SA-789.

A.2.9 Tubes and tube u-bends should typically not be heat treated after bending or straightening unless otherwise approved by purchaser. For standard grades, cold work shall be limited to 15 % maximum, which is equivalent to limiting U-bending bend radii to a minimum of 3.3 times the tube diameter (3.3D). For 25 % Cr and 27 % Cr DSSs grades, bends can be made down to 1.5D bend radii with no heat treatment required. If the hardness requirement given in A.2.4 is exceeded due to working or bending, re-solution annealing per A.2.3 will be required.

A.2.10 For Standard DSS with U-bend radii less than 3.3D, and if heat treatment is allowed or required by purchaser, the fabricator shall submit heat treatment plans for approval, which will include precautions to minimize the exposure of any sections to 700 °C to 950 °C (1300 °F to 1750 °F), as this could cause unacceptable intermetallic precipitation. The preferred heat treatment method is electric resistance, which is done for only seconds. Lubricants shall be removed from tube surfaces prior to heat treatment.

A.2.11 After initial solution annealing or any other heat treating, other than bright anneal procedures, all tubing shall receive a descaling treatment of pickling followed by a neutralizing and appropriate rinsing treatment. All mill scale shall be removed.

Annex B
(informative)

Example of Special Welding Procedure Qualification Requirements for DSSs

This Annex has been deleted. Recommended requirements are given in API 582.

Annex C
(informative)

Example of Special Welding and Fabrication Requirements for DSSs

This Annex has been deleted. Recommended requirements are given in API 582.

Annex D
(informative)

Example of a Duplex SS Casting Specification

D.1 General

D.1.1 Scope

This specification covers the material, testing, and inspection requirements for duplex stainless steel castings. This specification supplements ASTM A995 and is applicable for Grades 1B, 4A, 5A, and 6A (UNS J93372, J92205, J93404, and J93380). If any requirement of this document conflicts with ASTM A995 or other documents, the purchaser shall be notified for resolution.

D.1.2 Definitions

D.1.2.1 The term “purchaser,” as used in this specification, shall mean the Owner, or their representatives.

D.1.2.2 The term “vendor,” as used in this specification, shall include those who have been contracted to provide the specified materials.

D.1.2.3 A “heat lot” is defined as one heat treatment batch from the same heat, melt of material.

D.1.3 Referenced Documents

The following codes, standards, and specifications shall be considered as a part of this specification. All documents shall be the latest editions in force.

ASME Sect. VIII, *Boiler and Pressure Vessel Code*

ASNT-TC-1A, *Personnel Qualification and Certification in Nondestructive Testing*

ASTM A703, *Specification for Steel Castings, General Requirements for Pressure-Containing Parts*

ASTM A802, *Steel Castings, Surface Acceptance Standards, Visual Examination*

ASTM A903, *Steel Castings, Surface Acceptance Standards, Magnetic Particle and Liquid Penetrant Inspection*

ASTM A923, *Detecting Detrimental Intermetallic Phases in Wrought Duplex Austenitic/Ferritic Stainless Steels*

ASTM A995, *Castings, Austenitic-Ferritic (Duplex) Stainless Steel, for Pressure-Containing Parts*

ASTM E165, *Liquid Penetrant Inspection Method*

ASTM E433, *Standard Reference Photographs for Liquid Penetrant Inspection*

ASTM E562, *Determining Volume Fraction by Systematic Manual Point Count*

ASTM E1245, *Determining Inclusion Content of Steel and Other Metals by Automatic Image Analysis*

EN 10204, *European Standard, Metallic Products, Types of Inspection Documents*

MSS SP-54, *Quality Standard for Steel Casting for Valves, Flanges and Fittings and Other Piping Components, Radiographic Examination Metho*d

MSS SP-55, *Quality Standard for Castings for Valves, Flanges and Fittings and other Piping Components, Visual Method*

D.2 Process and Manufacture

D.2.1 Castings shall be made by one of the following processes:

a) electric arc or induction furnace melting followed by separate refining, such as vacuum oxygen decarburized (VOD) or argon oxygen decarburized (AOD);

b) electric induction furnace melting with virgin metal or refined ingots; melt shall be protected with slag or other means from atmospheric contamination or degassing. Foundry revert cannot be used without separate refining.

D.2.2 All castings furnished to this specification shall be solution annealed at 1120 °C (2050 °F) to 1150 °C (2100 °F) for 1.0 hours per 25 mm (1 in.) section thickness, with a minimum of 2 hours and water quenched to room temperature to obtain the required Duplex micro-structure. Prior to water quenching the casting may be furnace cooled from the solution annealing temperature to no lower than 1040 °C (1900 °F). The furnace to water quench time shall be less than 1 minute. Air cooling is not permitted.

D.2.3 The heat treatment of the castings shall be performed in-house by the foundry. Sub-contracting of the heat treatment needs purchaser's approval.

D.3 Chemical Composition and Tests

D.3.1 Composition

A certified product analysis of the casting is required and shall meet the limits required by ASTM A995, except that the minimum Nitrogen content shall be 0.15 %.

D.3.2 Tension Testing

Supplementary requirement S14 from ASTM A703 shall be required.

D.4 Ferrite Content

D.4.1 One specimen from each heat lot shall also be examined to determine the ferrite/austenite ratio.

D.4.2 The ferrite content shall be 35 % to 60 %. The ferrite content shall be determined by the manual point count in accordance with ASTM E562, minimum magnification shall be 500X. The maximum percent error, per E562, shall be 10 %. Alternatively, a computerized microstructural analysis per ASTM E1245, or any other method previously agreed to in writing by the purchaser, may be used.

D.5 Special Tests For Detrimental Intermetallic Phases

D.5.1 An impact test in accordance with the requirements in Table D.1 and D.5.3 is required for every melt and heat treatment lot. Exceptions require written approval of the purchaser. For castings with a net weight over 450 kg (1000 lb), both the impact test and corrosion test (per Table D.1 and D.5.2) are required in accordance with Table D.1.

Table D.1—Impact and Corrosion Test Requirements

UNS	Grade	ACI	Impact Test/ Temperature	Corrosion Test/ Temperature
J93372	1B	CD4MCuN	A370/–40 °C	A923C/40 °C
J92205	4A	CD3MN	A370/–40 °C	A923C/25 °C
J93404	5A	CE3MN	A370/–40 °C	A923C/50 °C
J93380	6A	CD3MWCuN	A370/–40 °C	A923C/50 °C

D.5.2 Corrosion Test

D.5.2.1 When required, one test specimen from each heat lot of material shall be tested in accordance with the requirements of Table D.1. Exemption by ASTM A923, paragraph 15 “Rapid Screening Test” is not permitted. The corrosion rate calculated from weight loss shall be reported in mdd ($mg/dm^2/day$). No pitting is allowed.

D.5.2.2 All specimens shall be prepared per ASTM A923, paragraph 18. Corrosion test specimens shall be machined from a section taken from, or representing the maximum cross-section of the casting. The maximum required sample section thickness is 150 mm (6 in). Mechanical deformation shall not have been performed on the corrosion specimen prior to testing. The corrosion test specimen shall have the same temperature as the test solution when placed into the ferric-chloride solution.

D.5.2.3 In the event a specimen does not meet the acceptance criteria, two new specimens from the given heat lot may be taken and retested. The purchaser must be notified before proceeding with retesting. These must meet the same acceptance criteria. If either retest specimen fails, the vendor has the option of re-solution annealing and retesting.

D.5.3 Impact Testing

D.5.3.1 One set of Charpy-V notch impact tests in accordance with Table D.1 is required for one sample from each heat lot. Location of all specimens shall be from the center of the maximum cross-section. Where feasible to prevent destruction of a usable casting, the impact specimens, full-size, may be removed from prolongations or extra stock.

D.5.3.2 The Charpy tests shall be performed at maximum –40 °C (–40 °F) and shall meet the requirements of 54 J (40 ft-lb), minimum.

D.6 Nondestructive Examination

D.6.1 General

D.6.1.1 Nondestructive examination shall be based upon ASME Code, Section V and the requirements given below. Also, Supplemental Requirements S6 and S10 from ASTM A995 shall be met.

D.6.1.1.1 For castings with a net weight over 450 kg (1000 lb), the purchaser shall approve in writing the proposed procedures prior to nondestructive examination.

D.6.1.1.2 For castings with a net weight over 450 kg (1000 lb), all personnel performing nondestructive examinations (NDE) shall be certified in accordance with ASNT SNT-TC-1A. Personnel interpreting or evaluating results of nondestructive examination for acceptance or rejection shall be certified to SNT-TC-1A Level II or Level III.

D.6.1.1.3 Equipment shall meet the requirements of and be calibrated in accordance with ASME Code, Section V.

D.6.2 Visual Inspection

All castings shall be visually inspected per MSS SP-55 or ASTM A802. For ASTM A802 acceptance shall be in accordance with Level II.

D.6.3 Liquid Penetrant Examination

D.6.3.1 Liquid penetrant examination is required for all castings.

D.6.3.2 Procedures for liquid penetrant examination (PT) shall be per ASTM E165.

D.6.3.3 The external surface, accessible wetted surfaces, and repairs require 100 % PT. Acceptance criteria shall be in accordance with ASTM A903 Level I.

D.6.4 Radiography

D.6.4.1 For all castings for pressure rating Class 1500 and higher, radiography is required of all critical areas and butt weld ends after the final heat treatment per ASTM A703, Supplementary Requirement S5.

D.6.4.2 Castings for rating Class 600 and 900 require radiography of all butt weld ends and of the critical areas of the pilot casting of each pattern after the final heat treatment per ASTM A703, Supplementary Requirement S5.

D.6.4.3 The acceptance shall be per MSS SP 54.

D.7 Repairs

D.7.1 Welding processes shall be SMAW or GTAW.

D.7.2 No autogenous welding is allowed.

D.7.3 Welding procedures (WPS and PQR) and welders shall be qualified per ASME Code, Section IX. This includes impact testing of full-size specimens at –40 °C (–40 °F) to meet minimum weld metal and heat affected zone impact energy of 34 J (25 ft-lb) and 54 J (40 ft-lb), respectively.

D.7.4 Filler metals for repair welds shall be selected based on Table D.2, below, and matching or overmatching fillers are allowed. For repairs requiring postweld heat treatment (solution annealing and water quenching), it is advised to consult with the welding consumables manufacturer for recommended filler metals, especially in critical services. There are special welding consumables made for castings.

Table D.2—Welding Consumables

Process	Grade 4A	Grade 1B, 5A and 6A
SMAW	SFA 5.4 E2209	SFA 5.4 E2553, E2594 or E2595
GTAW/GMAW	SFA 5.9 ER2209	SFA 5.9 ER2553, or ER2594
SAW	SFA 5.9 ER2209 with a flux designed for DSSs	SFA 5.9 ER2594 with a flux designed for DSSs
FCAW	SFA 5.22 E2209TX-X or EC2209	SFA 5.22 E2553TX-X, E2594TX-X, EC2553, or EC2594
NOTE This table does not cover some of the specialized 25 % Cr alloys and the material manufacturer's (i.e. the alloy supplier's) recommendations on welding consumables should be followed.		

D.7.5 Castings require post weld heat treatment (solution annealing) per D.2.2 after all major repair welding of Grade 1B, 4A, 5A, and 6A. PWHT (solution annealing) is also required for minor repair welding of wetted surfaces of Grade 1B, 5A, and 6A.

D.8 Certification

D.8.1 The vendor shall certify in writing that the castings meet the requirements of the latest edition of ASTM A 995 (including applicable supplementary requirements of ASTM A703) and this specification.

D.8.2 Certified copies of the material certifications meeting the requirements of ASTM and showing the results of all tests shall be furnished to the purchaser.

D.8.3 All certifications shall be signed by a responsible officer of the vendor, whose identity shall be legally displayed.

Annex E
(informative)

Example of a Hot Isostatically-pressed (HIP) Duplex SS Material Specification

E.1 General

E.1.1 Scope

This specification is informative and is to be used as a manufacturing guide for HIP'ed DSSs materials. The materials are covered by ASTM A988, and manufacturing practices and testing of material are included.

E.1.2 Definitions

Capsule – Container used for encapsulation and hot isostatic pressing of the powder.

Cross Contamination – An intermix of powder of different alloy type.

Filling tube – A tube on top of the capsule through which powder is filled.

HIP – Hot Isostatic Pressing.

Gas atomization – The process in which a melt is slushed into small particles in a controlled chamber. When the particles solidify, a metal powder where each particle has the same composition as the melt is formed.

QTC – Quality Test Coupon.

E.1.3 Referenced Documents

The following standards and specifications shall be considered as a part of this specification. All documents shall be the latest editions published.

ASTM A370, Standard Test Methods and Definitions for Mechanical Testing of Steel Products

ASTM A388, Standard Practice for Ultrasonic Examination of Steel Forgings

ASTM A923, Standard Test Methods for Detecting Detrimental Intermetallic Phase in Duplex Austenitic/Ferritic Stainless Steels

ASTM A988, Standard Specification for Hot Isostatically-Pressed Stainless Steel Flanges, Fittings, Valves, and Parts for High Temperature Service

ASTM E165, Standard Practice for Liquid Penetrant Examination for General Industry

ASTM E562, Standard Practice for Determining Volume Fraction by Systematic Manual Point Count

ASTM G48, Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution

DIN 50602, Metallographic examination; microscopic examination of special steels using standard diagrams to assess the content of non-metallic inclusions

EN 10204, European Standard, Metallic Products, Type of Inspection Documents

E.2 Material and Manufacture

E.2.1 Manufacturing Practice

E.2.1.1 The HIP'ed parts shall be manufactured from pre-alloyed powder. The powder shall be manufactured using a gas atomization process, where the melting process in use can produce a specific composition.

E.2.1.2 If powder blends from different heats are used, all blends shall fulfill the standard requirements. Powder blends shall also be mixed in such manner that a homogeneous blend is obtained, both in composition and particle size.

E.2.1.3 The powder shall be stored in such manner that it is not in contact with the direct environment and to avoid humidity and oxidation.

E.2.1.4 The HIP'ed part shall be manufactured from a homogeneous powder blend by filling a capsule with powder, evacuating the capsule and then sealing it thoroughly.

E.2.1.5 The material used to produce capsules shall not have a harmful effect on the DSSs material, e.g. low alloy carbon steel can be used. The capsules shall be cleaned of any type of dust or residue from the welding procedure.

E.2.1.6 The HIP'ing operation shall use adequate temperature, pressure and time to achieve full densification of the whole part to a solid compact.

E.2.1.7 The capsule plate can be removed by pickling or machining.

E.2.2 Chemical Composition

Both powder blend and the HIP'ed part shall have a chemical composition that conforms to the specified composition in ASTM A988.

E.2.3 Heat Treatment

E.2.3.1 Solution annealing followed by water quenching shall be performed. Components shall be placed so that free circulation around each component can be ensured during the heat treatment process, including quenching.

E.2.3.2 The heat treatment can be performed prior to, or after, removal of the capsule plate. If the capsule plate is removed prior to heat treatment, the process has to be performed in a protective environment.

E.3 Testing of Material Properties

E.3.1 Test Material

E.3.1.1 Material properties can be tested on elongations (such as fill stems) of HIP'ed component or on a QTC of adequate size that has been produced from the same powder heat and heat treated in the same batch as the HIP'ed component. A minimum of one test sample is required from each production batch, which is each powder batch and quench lot.

E.3.1.2 All test qualification shall be performed on a similar position in the test sample. $T/4$ (thickness/4) shall be used for parts >50 mm and $T/2$ for parts <50 mm, unless otherwise specified by buyer.

E.3.1.3 Densification shall be tested using argon analysis and on every single HIP'ed component at an adequate position.

E.3.2 Microstructure

E.3.2.1 The microstructure shall be investigated according to ASTM A923 Method A to determine the presence of deleterious precipitations. One specimen etched in 40 % sodium hydroxide solution shall be used for examination. The examination shall be performed using 400X to 500X magnification and the polish shall be performed to adequate finish.

E.3.2.2 Ferrite content shall be determined with the point count method according to ASTM E562. A similar specimen as in E.3.2.1 shall be used for examination. The ferrite content shall be within 40 % to 60 %.

E.3.2.3 Control of cross contamination shall be performed on etched material according to DIN 50602, Method K. The etching shall be performed with adequate procedure to discover possible cross contamination. Preferably, etching that is suitable for the duplex alloy shall be used. Cross contamination shall meet K3 < 10.

E.3.2.4 Control of non-metallic inclusions shall be performed on polished material according to DIN 50602, Method K. Polishing shall be of adequate finish for examination. Inclusion levels shall meet K3 < 10.

E.3.3 Mechanical Properties

E.3.3.1 Tensile testing shall be performed according to ASTM A370 and meet the requirements of ASTM A988 for the specific alloy.

E.3.3.2 Impact toughness shall be tested with Charpy-V notch testing according to ASTM A370 on one set (including 3 specimens) of each test sample. The test temperature shall be –46 °C (–51 °F) and the impact toughness shall be minimum 45J in average and minimum 35J on a single sample.

E.3.4 Corrosion Testing

E.3.4.1 Corrosion testing shall be performed according to ASTM G48 Method A.

E.3.4.2 Materials of 25Cr shall be tested at a temperature of 50 °C (122 °F) and exposure time 24h. After the test exposure, the specimen shall be pickled for 5 minutes at 60 °C (140 °F) in a solution of 20 % HNO_3 + 5 % HF. No pitting shall be observed in 20X magnification and weight loss shall be less than 4.0 g/m^2.

E.3.4.3 Materials of 22Cr shall be tested at a temperature of 25 °C (77 °F) and exposure time 24h. After the test exposure, the specimen shall be pickled for 5 minutes at 60 °C (140 °F) in a solution of 20 % HNO_3 + 5 % HF. No pitting shall be observed in 20X magnification and weight loss shall be less than 4.0 g/m^2 (0.0040 oz/ft^2).

E.3.5 Densification

Argon level shall be tested using gas chromatography, argon content shall be ≤ 0.05 ppm on materials atomized in nitrogen gas.

E.4 Non-Destructive Testing

E.4.1 Ultrasonic Testing

E.4.1.1 Ultrasonic testing is to be performed on the heat treated and pickled part. The testing shall be performed according to ASTM A388.

E.4.1.2 The component shall have a surface condition that is suitable for ultrasonic testing. Manual grinding may be required to ensure suitable conditions.

E.4.2 Liquid Penetrant Testing

If liquid penetrant testing is to be performed, it shall be performed on the heat treated, pickled and machined part. The testing shall be performed according to ASTM E165.

E.5 Finish and Appearance

The surface shall be ground to remove damaging edges and corners. The surface of all items shall be pickled.

E.6 Handling and Packing

Handling and packing must be done with care so that no contamination of other metallic materials is introduced to the component surface. All handling equipment in direct contact must be clean.

E.7 Certification

A certificate shall be written and submitted to the purchaser according to EN 10204 3.1 or 3.2, ASTM or other applicable material specification.

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