Use of Duplex Stainless Steels in the Oil Refining Industry

API TECHNICAL REPORT 938-C
SECOND EDITION, APRIL 2011

AMERICAN PETROLEUM INSTITUTE

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Downstream Segment

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Introduction

Duplex stainless steels (DSS) are finding increasing use in the refining industry, primarily because they often offer an economical combination of strength and corrosion resistance. These stainless steels (SS) 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. The benefits expected from the use of DSS are maintained even to a ratio of 75/25 ferrite/austenite volume fraction (except for possible problems with weldability). Most refinery applications where DSS are used are corrosive, and DSS or other higher alloys are required for adequate corrosion resistance. However, some plants are also starting to consider DSS as a "baseline" material. [1] They are using it in applications where carbon steel may be acceptable, but DSS have been shown to be more economical considering their higher strength and better long-term reliability.

DSS 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). Figure 1 shows a comparison of some DSS with various austenitic SS showing the difference in strength and chloride corrosion resistance [expressed as pitting resistance equivalent number (PREN)]. [2] This chart shows the excellent combinations of higher strength and corrosion resistance available with DSS. It also shows that there are "subfamilies" of specific grades within both the DSS and austenitic families. This is also illustrated in Table 1.

DSS 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] Hence, the initial applications were almost exclusively heat exchanger tubing, particularly in corrosive cooling water services, and shafting or forgings. In the 1980s, second generation DSS became commercially available which helped overcome the problems at the welds. These new grades had nitrogen additions, which along with improved welding practices designed for the DSS, led to the welds' mechanical (strength and toughness) and corrosion properties being comparable to the annealed base metal. The DSS most commonly used today in refineries include those with 22 % and 25 % Cr. The 25 % Cr (super duplex grades) usually also contain more molybdenum and nitrogen, and so have higher PREN values than the 22 % Cr duplex steels.

Table 1 lists the chemistries and UNS numbers of various common DSS, including some first generation DSS for comparison. Note that UNS S32205 is a "newer version" of UNS S31803 and is produced with higher nitrogen, chromium, and molybdenum contents. ASME and ASTM standards for these grades are given in Table 2, while Table 3 provides the mechanical properties. Type 316L and other austenitic SS are included 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 DSS within refineries.

Use of Duplex Stainless Steels in the Oil Refining Industry

1 Scope

This report covers many of the "lean," "standard," and "super" grades of duplex stainless steels (DSS) 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 S31803 and S32205, while the super grades include S31260, S32520, S32550, S32750, S32760, S39274, and S39277. The grades which are labeled as "semi-lean" include S32304 and UNS S32003, have either lower Cr or Mo than the standard grades, and are used in some process services that are less aggressive. These alloys and lean duplexes, such as S32101, have also been used for storage tanks and structural applications primarily for their higher strength 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 DSS for tanks is addressed by API 650, Appendix X. Later revisions of this report may consider expanding the scope to include castings and other product forms for pumps, valves, and other applications. Use of DSS as a cladding is also not included within the scope of this document.

The majority of refinery services where DSS 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;

b) water, containing chlorides, with or without hydrocarbons; or

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

The specific plant locations containing these services are described in a later section and the report scope will be limited to these environments.

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 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*

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[1] ASME International, 3 Park Avenue, New York, New York 10016-5990. www.asme.org.

Table 1—Chemical Compositions of Commonly Used DSS and Other Alloys Composition, Mass % [a, e]

UNS Number	Type [b]	Cr	Mo	Ni	N	Cu	C	Mn	P	S	Si	Min PREN [d]	Other
First Generation DSS													
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	—
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	
Lean and Semi-lean DSS													
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	—
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	—
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	—
Standard DSS													
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	—
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	—
25 % Cr and Super DSS													
S31200	—	24.0 to 26.0	1.2 to 2.0	5.5 to 6.5	0.14 to 0.20	—	0.030	2.00	0.045	0.030	1.00	30.2	
S31260	—	24.0 to 26.0	2.5 to 3.5	5.5 to 7.5	0.10 to 0.30	0.20 to 0.80	0.030	1.00	0.030	0.030	0.75	34.0	W: 0.1 to 0.5
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	
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	—
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	—
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	37.9 [d]	W: 0.5 to 1.0

Table 1—Chemical Compositions of Commonly Used DSS and Other Alloys Composition, Mass % [a, e] (Continued)

UNS Number	Type [b]	Cr	Mo	Ni	N	Cu	C	Mn	P	S	Si	Min PREN [d]	Other
S32950	—	26.0 to 29.0	1.0 to 2.5	3.5 to 5.2	0.15 to 0.35	—	0.030	2.00	0.035	0.010	0.60	31.7	
S39274	—	24.0 to 26.0	2.5 to 3.5	6.0 to 8.0	0.24 to 0.32	0.20 to 0.80	0.030	1.00	0.030	0.020	0.80	38.6	W: 1.5 to 2.5
S39277	—	24.0 to 26.0	3.0 to 4.0	6.5 to 8.0	0.23 to 0.33	1.20 to 2.00	0.025	0.80	0.025	0.002	0.80	38.9	W: 0.8 to 1.2
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	29.5	—
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	33.8	
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 and in ASTM A240, 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. Note that UNS S32760 which has a minimum PREN of 40 required by the 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.

Table 2—ASME ad ASTM Specifications for DSS

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
Testing	ASTM A923

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

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	¾
S32101	2101	650	95	450	65	30.0	290	¾
S32003	2003	620	90	450	65	25.0	293	31
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	—
S31603	316L	485	70	170	25	40.0	217	95 R_b

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

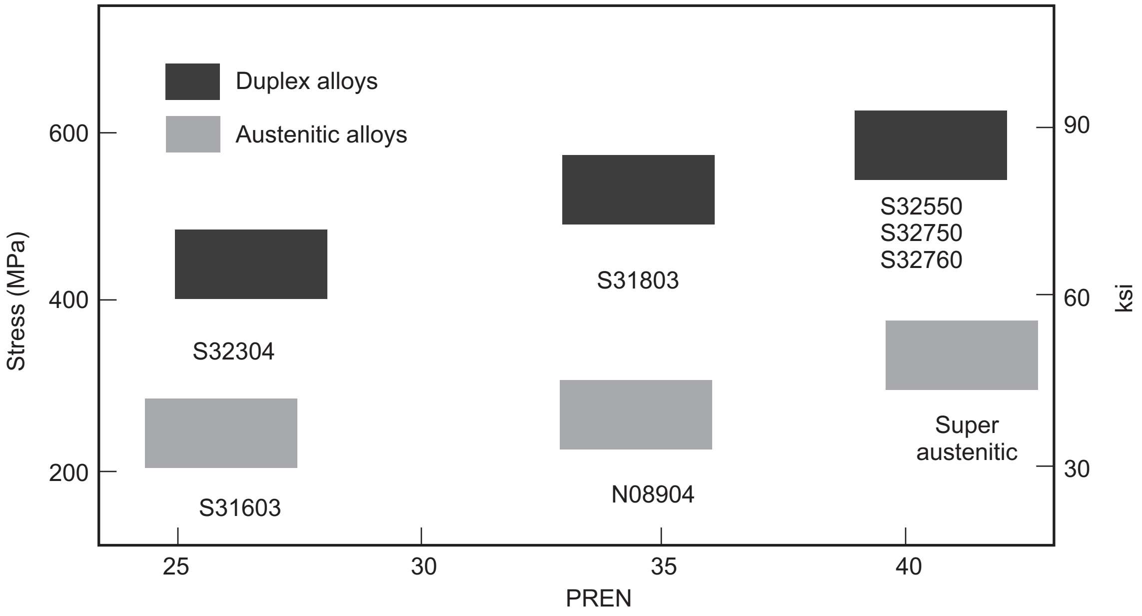

Figure 1—Comparison of the Proof Stress and Pitting Resistance of Duplex and Austenitic SS [2]

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*

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

ASTM E140, *Standard Hardness Conversion Tables for Metals Relationship Among Brinell Hardness, Vickers Hardness, Rockwell Hardness, Superficial Hardness, Knoop Hardness, and Scleroscope 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 Procedure for Calibrating Magnetic Instruments to Measure the Delta Ferrite Content of Austenitic and Duplex Austenitic-Ferritic 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 TM 0177, *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 19428-2959. www.astm.org.

[3] American Welding Society, 550 N.W. LeJeune Road, Miami, Florida 33126. www.aws.org.

[4] NACE International (formerly the National Association of Corrosion Engineers), 1440 South Creek Drive, P.O. Box 218340, Houston, Texas 77218-8340. www.nace.org.

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 DSS, 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 melted filler metal diluted with some melted base metal.

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
EDS	energy dispersive spectroscopy
ESR	electro-slag re-melt
FCAW	flux-cored arc welding
FCC	fluidized catalytic cracking
FCCU	fluidized catalytic cracking unit

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[5] National Institute of Standards and Technology, 100 Bureau Drive, Stop 3460, Gaithersburg, Maryland 20899-3460. www.nist.gov.

FN	ferrite number
GMAW	gas metal-arc welding
GTAW	gas tungsten-arc welding
HBW	Brinell hardness number (using specific test equipment)
HRC	Rockwell C hardness number
HRSG	heat recovery steam generator
HSC	hydrogen stress cracking
HV	Vickers hardness number
JIP	joint industry sponsored research project
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
SEM	scanning electron microscope
SMAW	shielded metal-arc welding
SS	stainless steel
SSC	sulfide stress cracking
SWS	sour water stripper
TWI	The Welding Institute
UT	ultrasonic testing
VAR	vacuum arc re-melt
VOD	vacuum oxygen decarburized
WPS	welding procedure specification

4 Metallurgy of DSS

4.1 Background

To address the interaction between proper specification of the materials and proper fabrication and welding practices in obtaining the expected toughness and corrosion resistance, an understanding of the metallurgical structure of DSS and the effects of various treatments on that structure is needed. Therefore, the metallurgy of the DSS is one of the first topics covered in this report. The subsequent discussion covers the resistance of DSS 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 DSS 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

DSS solidify as a fully ferritic structure and then form austenite within the ferritic structure with further cooling. Nitrogen promotes austenite formation from the ferrite at a higher temperature. This allows the desired phase balance to develop quickly at temperatures high enough to enable the diffusion of all elements closer to their preferred equilibrium positions during initial solidification. This favorable effect occurs during solidification, as in casting and welding, and in annealing and other high temperature exposures such as the HAZ of welds.

4.3 Problems to be Avoided During Welding

There are two primary problems to be avoided when welding DSS, as follows:

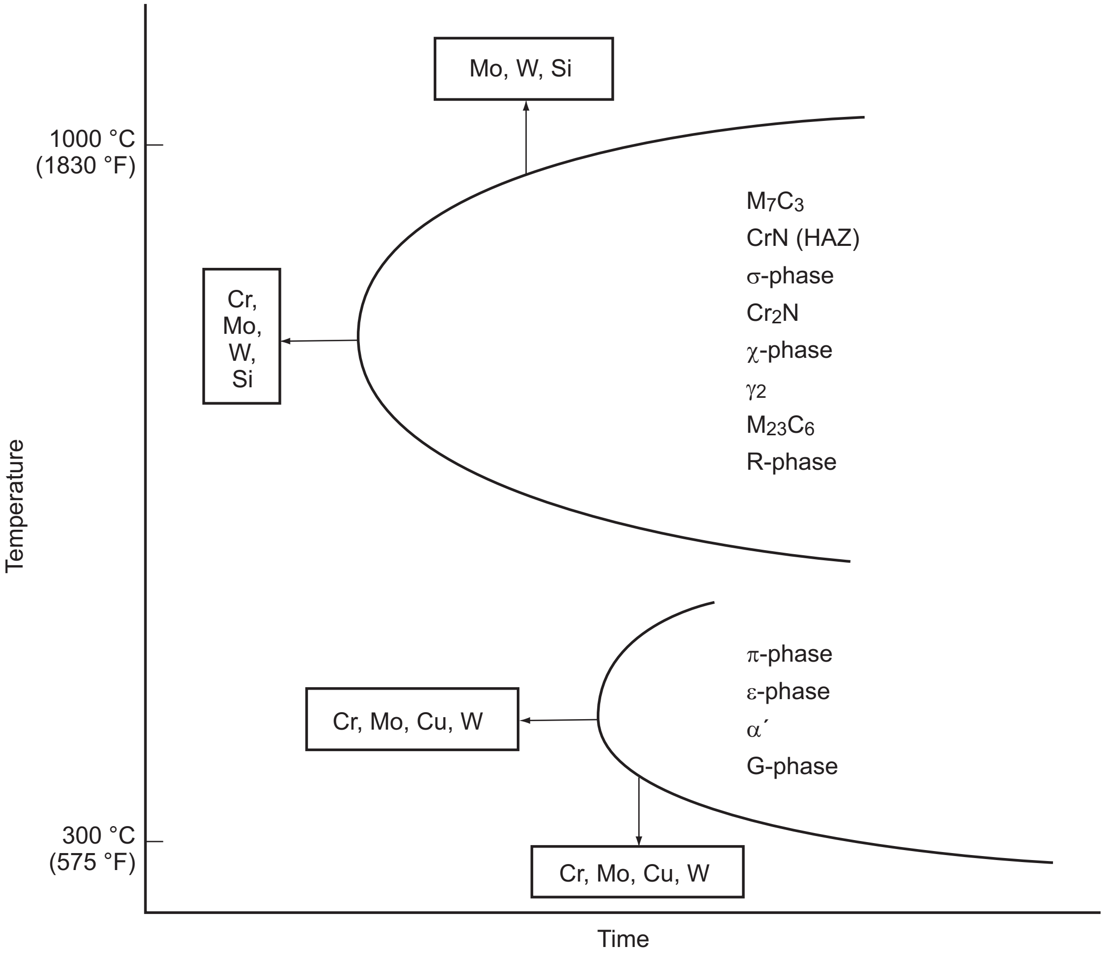
1) excessive ferrite in the HAZ or weld deposit,

2) the formation of harmful intermetallic phases 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 DSS 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 DSS 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.

This risk can be overcome by welding practices such as preheat or heat input, which counteract the tendency to excessively fast cooling of the weld and HAZ. Suggested limits on the ferrite content in weld and HAZ (appropriate for most refinery applications) are given in Section 6, Annex B, and Annex C. Mockups are typically required for tube-to-tubesheet welding procedure qualification.

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. Intermetallic phases, such as sigma phase or chi phase, are complex compounds of iron, chromium, and molybdenum. They are



NOTE: Similar curves are also shown in Figure 12, which shows the different curves for different grades of DSS.

Figure 2—Possible Precipitations in DSS [2]

extremely detrimental to corrosion resistance and toughness. 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:

— for a 22 % Cr DSS with nitrogen >0.14 %, about 30 to 60 minutes of exposure at 870 °C (1600 °F) will result in a significant loss of corrosion resistance and toughness;

— a 25 % Cr DSS will show similar degradation after 5 to 10 minutes at 850 °C (1560 °F);

— lean DSS such as S32304, are much more tolerant of time in this temperature range, and can be exposed for 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). Suggested limits are given in Annex C. 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

DSS 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 B31.3 Code and –29 °C (–20 °F) for some cases in the ASME Code Section VIII. These limits have qualifiers involving thickness, etc., and lower temperatures can be used by impact testing the material. Hence, actual limits are determined by reviewing the applicable Code.

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. [5] 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 DSS in refinery services.

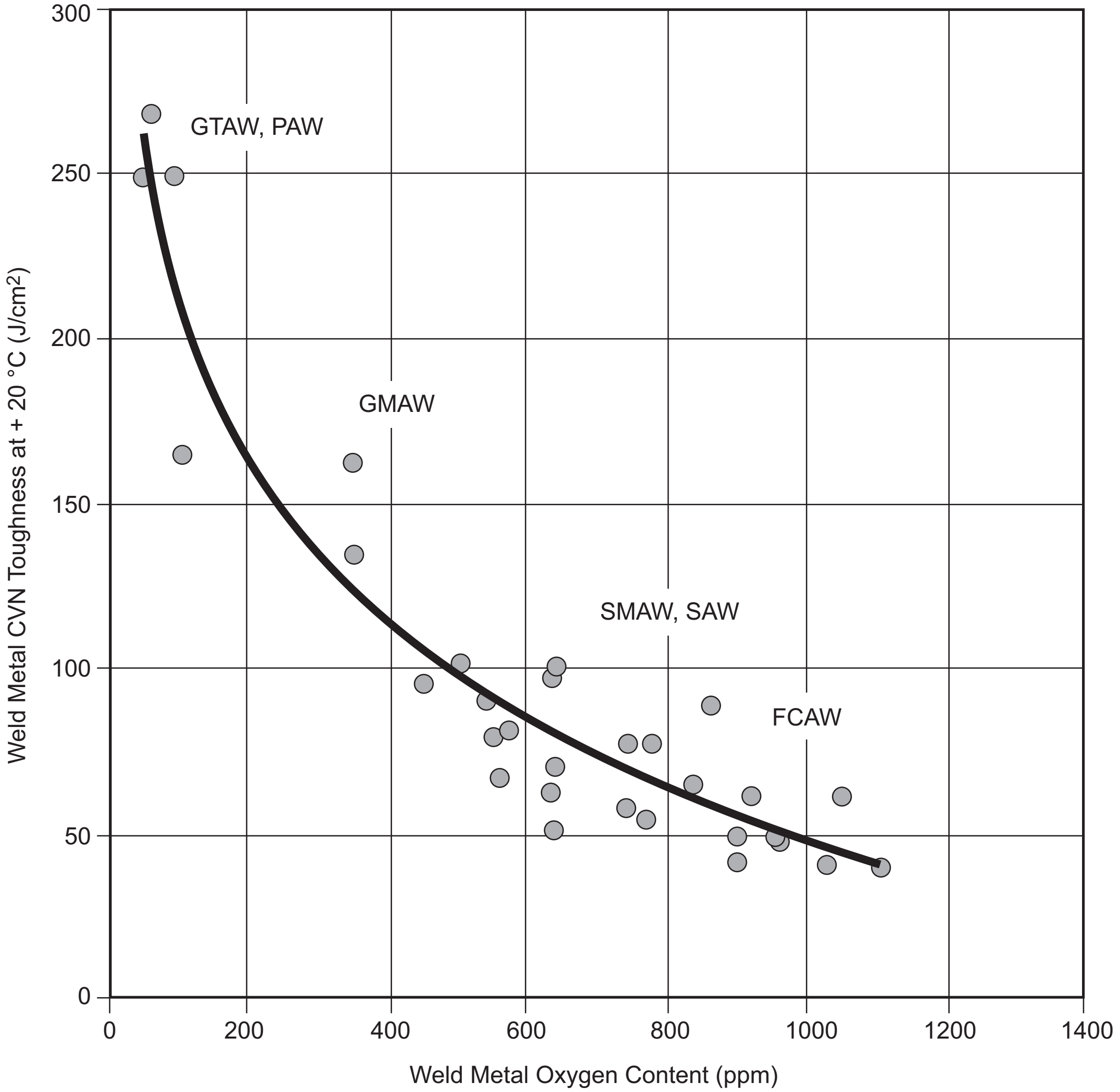


Figure 3—Effect of Weld Metal Oxygen Content on the Toughness of the Weld [5]

The ASME Section VIII requirements for impact testing for DSS base and weld metals are given in UHA-51(d)(3). They require impact testing of all DSS thicker than 10 mm ($^3/_8$ in.) or those with an MDMT less than –29 °C (–20 °F).

The maximum operating temperatures are limited by the susceptibility of the ferritic phase to 475 °C (885 °F) embrittlement (see 5.6). 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 this problem (Table 4). This Code limit applies to the risks associated with continuous long-term exposures above the limiting temperature. It also applies to actual metal temperature, not process stream temperature. Brief infrequent excursions of the actual metal temperature into the embrittlement range may be tolerated without significant loss of properties; however, the damage from overheating is cumulative. The Code does not address the issue of excursions. Some refiners are interested in having allowances added to the Codes for short-term operation at higher temperatures such as 340 °C to 425 °C (650 °F to 800 °F). This may be an action item to be pursued by API committees.

Table 4—ASME Code Maximum Allowable Temperatures, °C (°F)

Grade	ASME Section VIII (Div. 1)	ASME B31.3
S32304	316 (600)	316 (600)
S32101	316 (600) Code Case 2418	NL
S32003	343 (650) Code Case 2503	343 (650) Code Case
S31803 (Note 1)	316 (600)	316 (600)
S31200	316 (600)	NL
S31260	343 (650)	NL
S32550	260 (500)	NL
S32750	316 (600)	316 (600)
S32760	316 (600) Code Case 2245	316 (600)

NOTE NL = not listed

1) S32205 can use the design allowables for S31803 and the material should be dual-certified.

The hardness conversions between the Rockwell C and Vickers scales is different for DSS compared to CS and other low-alloy, ferritic steels. [2] This is an important consideration when hardness limits from industry standards which are given in Rockwell C are applied to weld procedure qualifications, for which Vickers is a practical hardness testing method. The conversion chart given in ASTM E140 is often used, and while this chart is acceptable for CS and low-alloy steels, it results in a conservatively low Vickers criteria for DSS. 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 DSS should use 334 HV. Also relevant for microhardness measurements is the possibility that the size and even the orientation of the two phases may be coarse relative to the indenter in certain products such as cast DSS.

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.

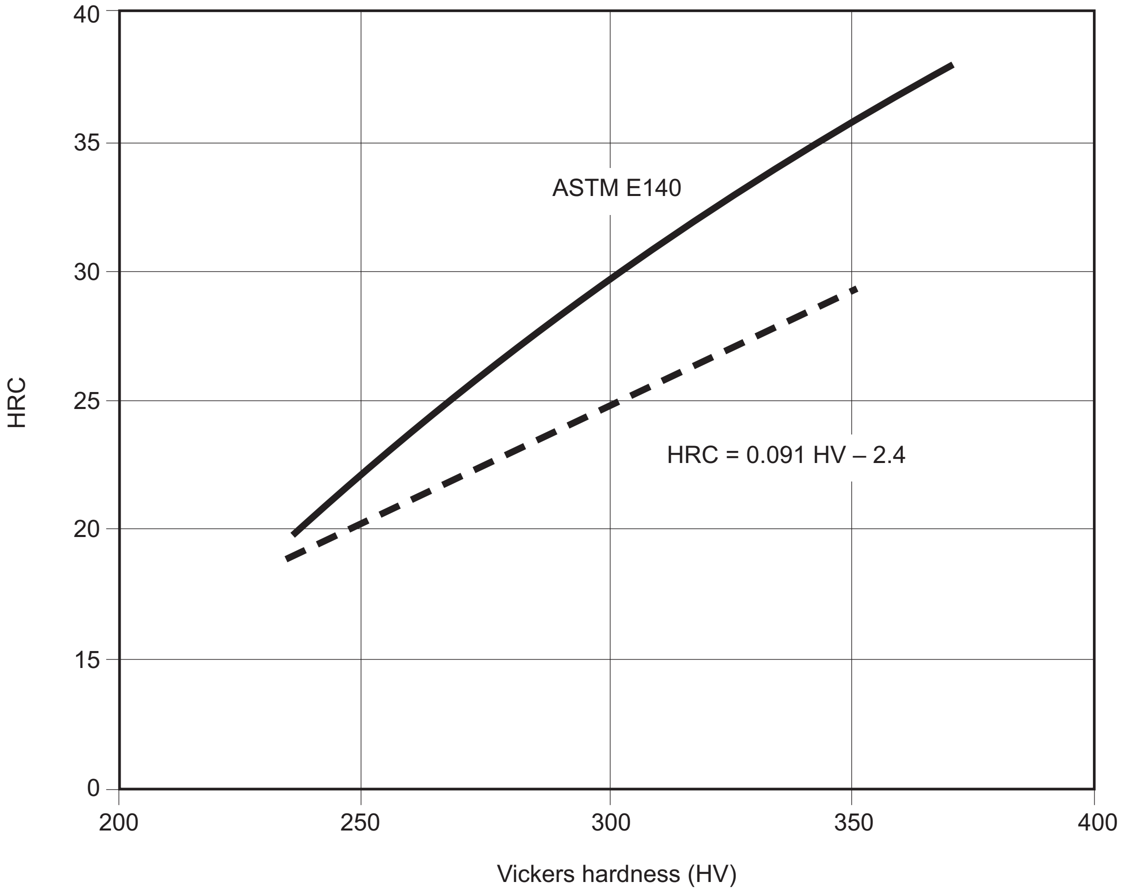


Figure 4—Compilation of Hardness Data for a Range of Duplex Parent Materials and Weldments Showing the Best-fit Line and ASTM E140 Conversion for Ferritic Steel [2]

5 Potential Environmentally-related Failure Mechanisms

5.1 Chloride Pitting and Crevice Corrosion

Because DSS are generally designed with higher Cr levels than the austenitic stainless grades, and because the duplex grades readily accept alloying with molybdenum and nitrogen, most DSS 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.

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

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

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 DSS, the two phases will have partitioning of the alloying elements, and hence, can have a different PREN for each phase. For most DSS material from experienced suppliers, this has not been a significant problem as these suppliers strive to balance the PREN between the two phases. Some examples of alloy partitioning for 25 Cr DSS are shown in Table 5. [6] [17]

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 A) 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 CPT tests in ferric chloride on various duplex and austenitic SS, are shown in Figure 5. [8] 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] Typical specifications for CPT minimum values are 20 °C (68 °F) for S32205 weld deposits and 35 °C (95 °F) for the super duplex weld deposits.

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

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

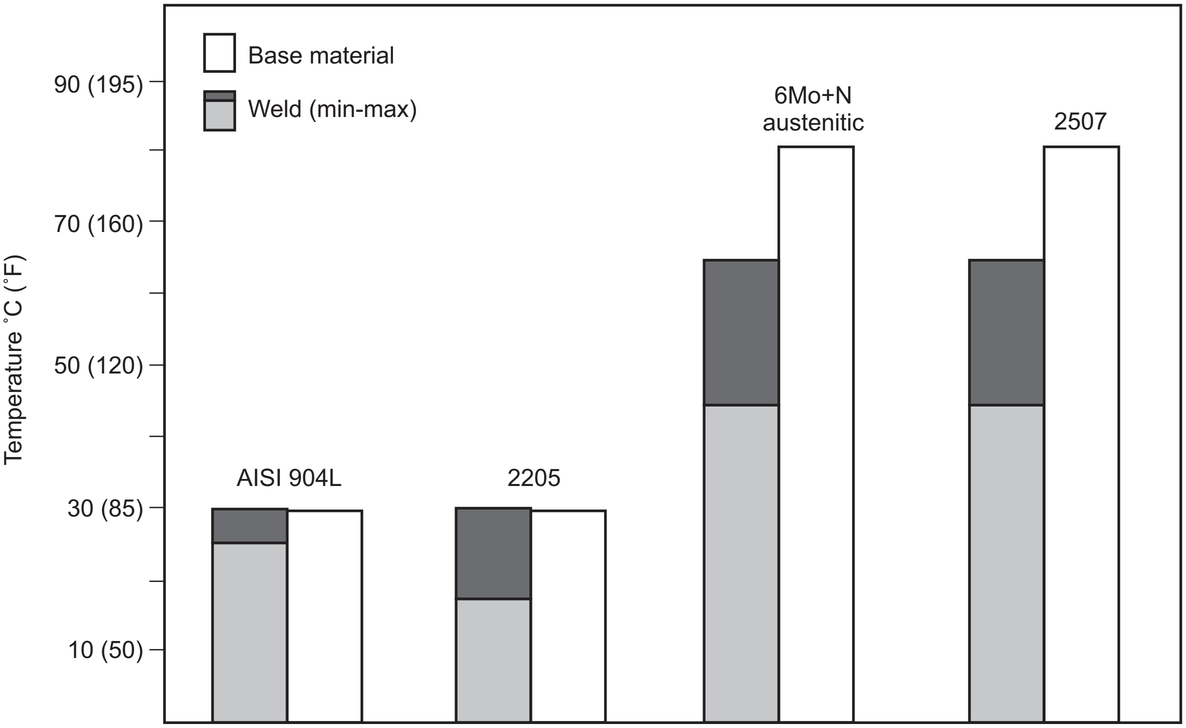


Figure 5—CPT for 22 % Cr and 25 % Cr DSS Alloys Compared to Austenitic SS Alloys in 6 % $FeCl_3$, ASTM G48 Test Method A [8]

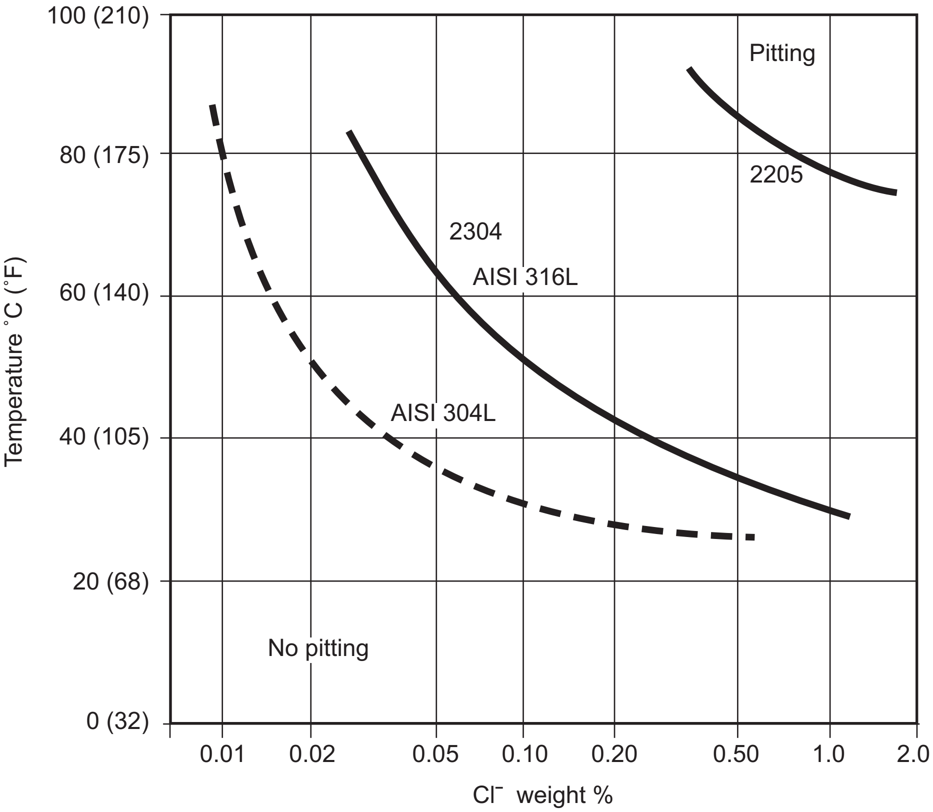


Figure 6—CPTs at Various Concentrations of Sodium Chloride (at +300 mV vs. SCE, Neutral pH) [8]

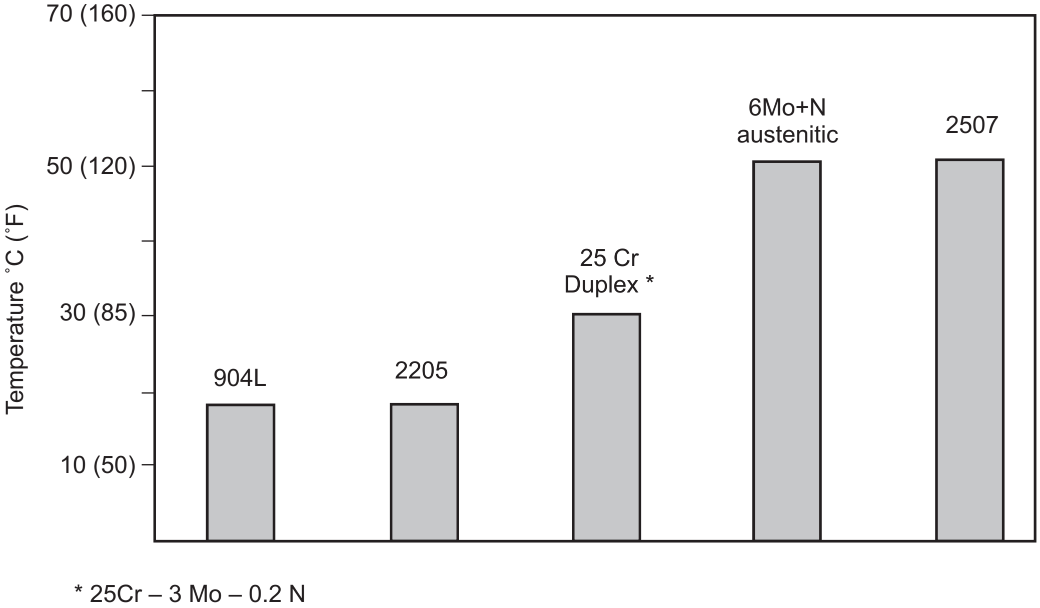


Figure 7—CCTs for 22 % Cr and 25 % Cr DSS Alloys Compared to Austenitic SS Alloys in 6 % $FeCl_3$, ASTM G48 Test Method B [8]

The super duplex SS grades (PREN ≥40) have shown excellent resistance to general and localized corrosion resistance in polluted and unpolluted seawater. They can be considered as being immune to stress corrosion cracking in seawater service (see 5.2). These alloys also possess good erosion resistance in sea water heat exchanger tubing applications when exposed to 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 for super duplex SS grades is lower with chlorinated sea water than in natural sea water. A typical limit is 60 °C (140 °F) at flow velocities of 1.5 m/s (5 ft/s) minimum. An additional requirement is that in-coming seawater should be filtered in order to reduce silt and sand deposits that promotes corrosion.

5.2 Chloride Stress Corrosion Cracking (CSCC)

The risk of CSCC restricts the use of standard austenitic SS grades such as 304L and 316L. Depending on the chloride concentration (together with the opportunity for further concentration on a hot surface), actual metal temperature, acidity/pH, tensile stress, time of exposure, and oxygen content, this mechanism can cause rapid failures. In most cases, temperatures greater than 60 °C (140 °F) are needed for cracking of austenitic SS, with cracking tendency increasing with increasing metal temperature. However, CSCC is dependent upon all of the listed factors being present, and the absence of any one of them can effectively block SCC.

DSS are a common "replacement" or alternative material in services where the threat of CSCC makes 300 series SS a poor or marginal alloy choice. Practical experience and laboratory testing have shown the good resistance of DSS to CSCC, but they are not immune. [8] [25] Figure 8 and Figure 9 present results from tests that compared various grades of DSS 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 pH 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 DSS have a much higher resistance to SCC than austenitic SS.

Additional considerations for predicting susceptibility of a DSS to CSCC include:

a) chloride concentration can build up under boiling conditions, or in the water film in contact with a heat-rejecting surface;

b) high pH environments such as those containing NH_4HS, 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 sea water splashing which operate above 100 °C [212 °F]) [26]; and

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

There have been a few reported cases of cracking in the industry, but most are under severe conditions where SCC could be predicted. Some of these 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 DSS 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 SCC of a 2 % Cr DSS in a crude unit application shown in Table 7.

Other examples from refinery services reported in NACE Refin-Cor (Table 6) are described in 5.2.1 through 5.2.3. Additional cases relating to improper fabrication have also been reported.

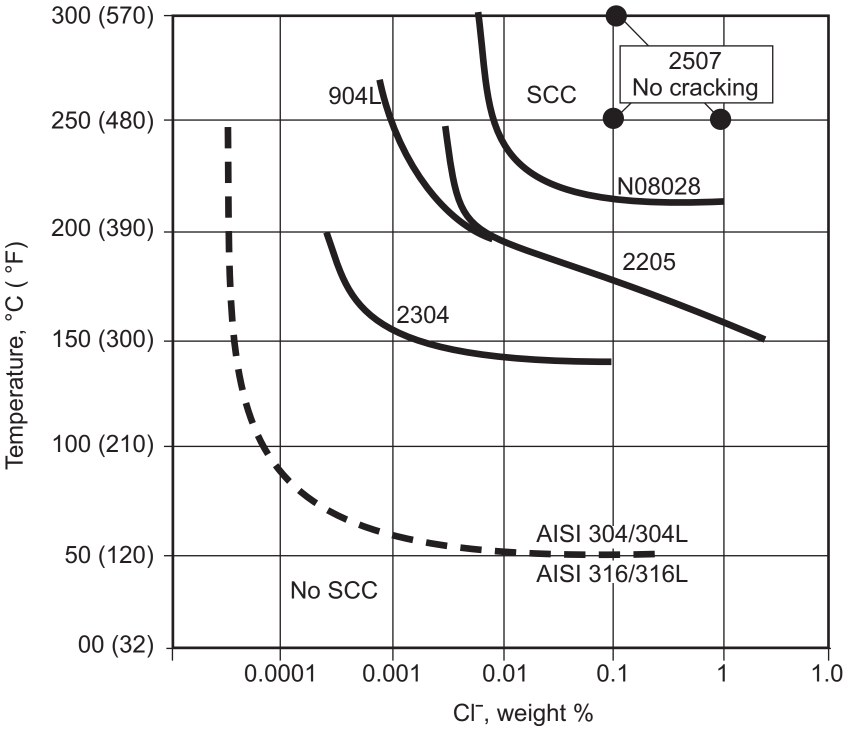


Figure 8—CSCC Resistance of 22 % Cr and 25 % Cr DSS Alloys Compared to Austenitic SS Alloys in Oxygen-bearing Neutral Chloride Solutions [8]

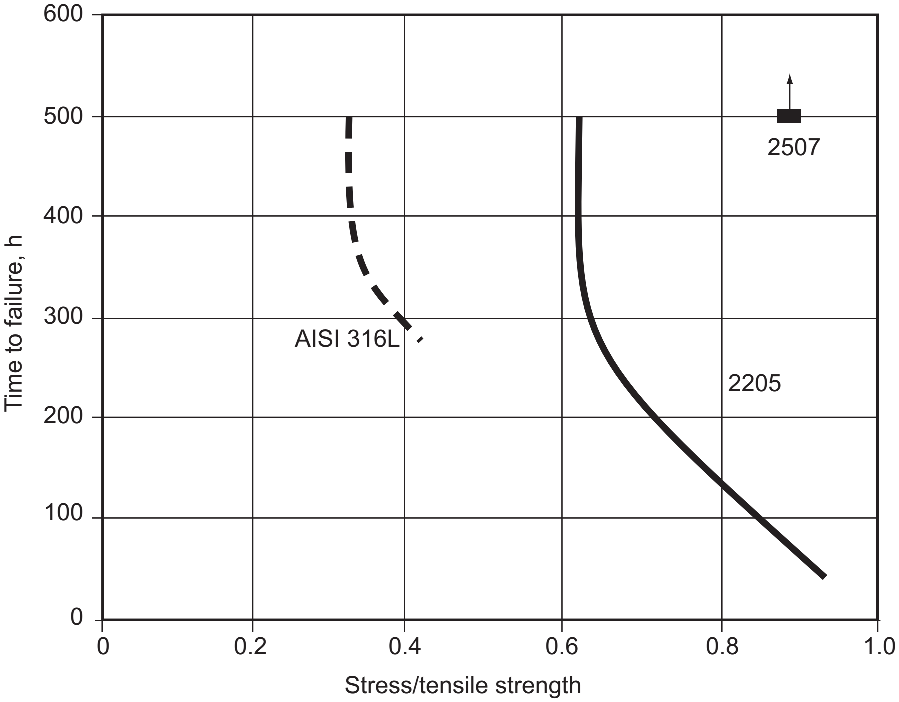


Figure 9—Results of SCC Tests of 22 % Cr and 25 % Cr DSS Alloys Compared to Austenitic SS Alloys in Constant Load Tests in 40 % $CaCl_2$, 1.5 pH at 100 °C with Aerated Test Solution [8]

5.2.1 98F5.5-04: FCCU and Light End Recovery

This case describes experiences with twisted 2205 SS tube failures in the overhead of a diluent recovery unit. It was discovered that the tubes had suffered CSCC that lined up with the residual stress patterns predicted in the tubes. The diluent recovery overhead is acidic due to chlorides and is neutralized with ammonia. CSCC was also found on the ID because the cooling water is recovered process water, which has significant chloride levels.

NOTE A dilute recovery unit is similar to a distillation unit.

5.2.2 98F5.8-01: Hydrocracker Unit

This is an example of CSCC in duplex 3RE60 SS in a hydroprocessing unit in which deposits occurred. Operating temperatures were around 149 °C to 204 °C (300 °F to 400 °F) where deposits collected.

5.2.3 98F5.8-02: Hydrodesulfurization Unit

This unit also experienced cracking of 2205 SS under ammonium chloride deposits operating at 130 °C (266 °F) in a hydroprocessing unit. This occurred only in areas in the exchanger where deposits could collect, while the balance of the exchanger was in pristine condition.

5.3 Hydrogen Stress Cracking/SSC

Many services where DSS are used in refineries involve a water phase containing H_2S, and hence, there is a risk of HSC. One form is sulfide stress cracking (SSC), which can occur in high-strength (hard) zones of base materials or welds. Numerous fabrication requirements can be specified to minimize hardness and hence, susceptibility to these cracking mechanisms. There has also been extensive testing done on DSS resistance to avoid these problems. 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 the 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.

NACE MR0175/ISO 15156 [9] gives varying PREN, temperature, H_2S partial pressure, and sometimes chloride limits for different grades of DSS to prevent SSC. These limits were developed specifically for the production industry, and were based on experience and laboratory testing focused on producing environments. Refining environments have some significant differences in pH, other contaminants, etc., and hence, the NACE MR0175 limits are not always applicable. Refining applications of DSS have often exceeded, sometimes significantly, the H_2S partial pressure limits in NACE MR0175, and the DSS have provided good resistance. This is a reflection of the differences between refining and producing environments.

A newer NACE standard (MR0103-2007) [10] is similar to older versions of NACE MR0175 but is targeted for the refining industry. It limits DSS base materials in severe wet sour services are 28 HRC maximum hardness. It also limits ferrite content to 35 to 65 volume percentage for weld procedure qualification, but that was based on earlier versions of this document (API 938-C). Some welding restrictions are also given including thickness and heat input limits.

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 [11] test for SSC, most DSS do not show any cracking until the applied stress is well above the proof strength. Cold work decreases the threshold failure stress. Figure 10 shows suggested chloride and H_2S partial pressure limits for S31803 and S32760 based on testing by TWI. [2]

There have been SSC failures in refinery applications; however, they have been attributed to improper fabrication. The hardness limit of 310 HV average (320 HV max) for weld procedure qualification given in Annex B, along with the

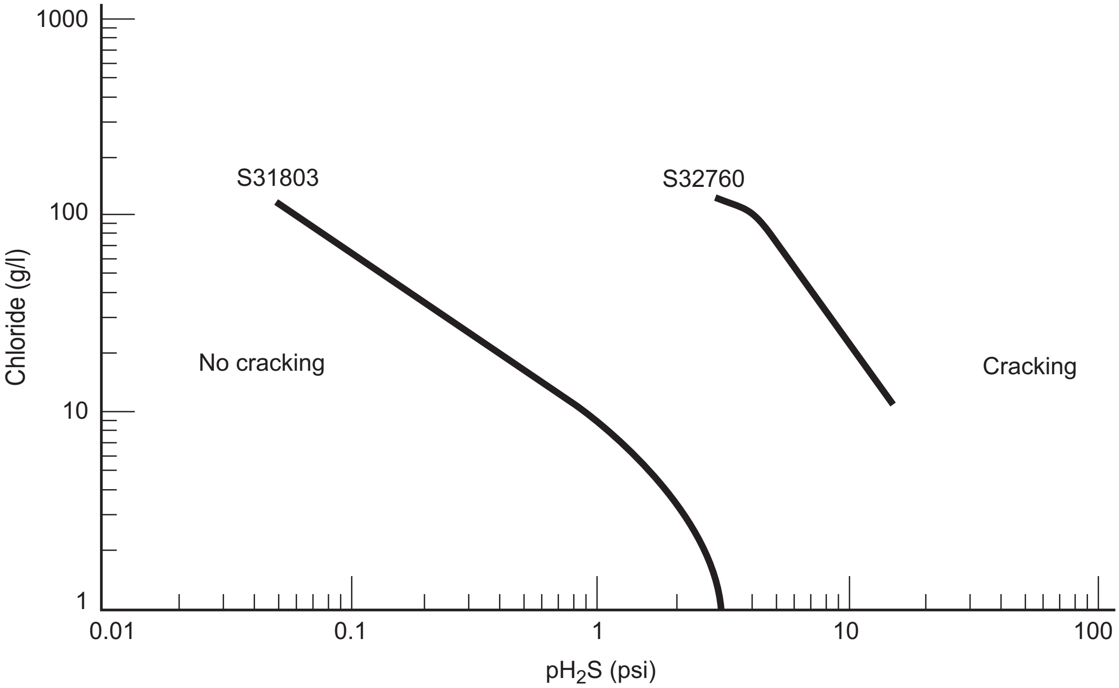


Figure 10—Suggested Chloride and pH_2S Limits for Cold Worked (34 HRC to 35 HRC) 22 % Cr (S31803) and a Super DSS (S32760) (pH < 4) [2] (1 psi = 6.89 kPa)

tight control of welding variables to help ensure that the production welding matches the qualified procedures, are the primary means of minimizing the risk of HSC/SSC. The 25 % Cr DSS require a higher limit due to their higher yield strength, and testing indicates they are acceptable to higher values.

5.4 Ammonium Bisulfide Corrosion

There is little or no published laboratory data showing the resistance of DSS to ammonium bisulfide environments, but there is extensive experiential data. Case histories come from hydroprocessing units, sour water strippers, FCC and coker units. Duplex 2205 is one of the commonly-used alloys for REACs under relatively severe conditions and is considered to be just slightly below Alloy 825 in resistance. [12] [13] Another good reference on use of DSS in REACs is API 932-B.

There are numerous case histories of DSS applications in hydroprocessing units with ammonium bisulfide (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 DSS 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 initiated in March 2000 concluded the initial phase of work in February 2003, and second and third phases shortly after. [14] Results of this work have better defined the role of several key variables on the corrosion behavior. [14] Some new applications have used 9.1 m/s (30 ft/s) as the maximum velocity for DSS; however, this limit may be conservative in many cases.

One case of DSS failing due to NH_4HS corrosion in a sour water stripper is listed in Table 7; however, the concentration was not reported.

In air coolers with a risk of wet ammonium chloride salt deposits, DSS could be susceptible to chloride pitting as discussed above. 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. [15]

5.5 Naphthenic Acid Corrosion

There are little or no published laboratory data and no documented experiential data for DSS in naphthenic acid refining services. However, some industry materials experts believe it would be acceptable because of its alloy content, especially molybdenum, and some applications are currently being installed. Naphthenic acid corrosion occurs primarily in crude units due to organic, carboxylic acids in the crude and various 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.

In most susceptible areas, 317L SS has been used and has displayed excellent resistance, but there are some services where 317L SS has not performed adequately or is deemed undesirable. Examples of the latter are heat exchangers 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 a risk of CSCC. DSS will have superior CSCC resistance, but would be limited to 260 °C to 340 °C (500 °F to 650 °F) based on Code limits (Table 4).

Molybdenum content is important for naphthenic acid corrosion resistance with 2.5 % minimum needed in most cases. In comparing the two grades of 22 % Cr duplex (UNS S31803 and S32205) to 317L SS with 3.0 % to 4.0 % Mo, the S32205 grade with 3.0 % to 3.5 % Mo should have at least equal resistance. The S31803 grade with 2.5 % to 3.5 % Mo would also be acceptable. It would be better than 316L SS, and equivalent to 316L special ordered with 2.5 % minimum Mo. Most 25 % Cr super DSS alloys have 3.0 % minimum Mo.

Partitioning of the molybdenum between the two phases could affect the overall naphthenic acid corrosion resistance. Table 5 shows some examples of partitioning in 25 % Cr alloys, and the molybdenum level varies, but is sufficient in both phases.

Table 5—Partitioning of Alloying Elements Between Phases

A—In 25 % Cr Alloys

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). [6]

[b] Chemical composition and PREN numbers of individual phases of 25-7-4 quench-annealed at 1075 °C (1967 °F). [6]

B—In 22 % Cr Weld Metals (Approx. Wt. %) [17]

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

Table 5—Partitioning of Alloying Elements Between Phases (Continued)

C—In 22 % Cr Base Metal and SMAW Weldments with Varying Arc Energy (Wt. %)				
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. [17]

D—In 22 % Cr Base Metal and GTAW Weldment (Wt. %) [17]				
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

5.6 475 °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 DSS. 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 for the Code temperature limits in the 260 °C to 340 °C (500 °F to 650 °F) range, and shows that the DSS 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 by Figure 11 and Figure 12. [2] [16] The 25 % 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) or >10,000 hours at 300 °C (570 °F).

475 °C (885 °F) embrittlement will occur more rapidly in weld metals than in base material, and hence, welded structures need to be limited to less time in the embrittlement range.

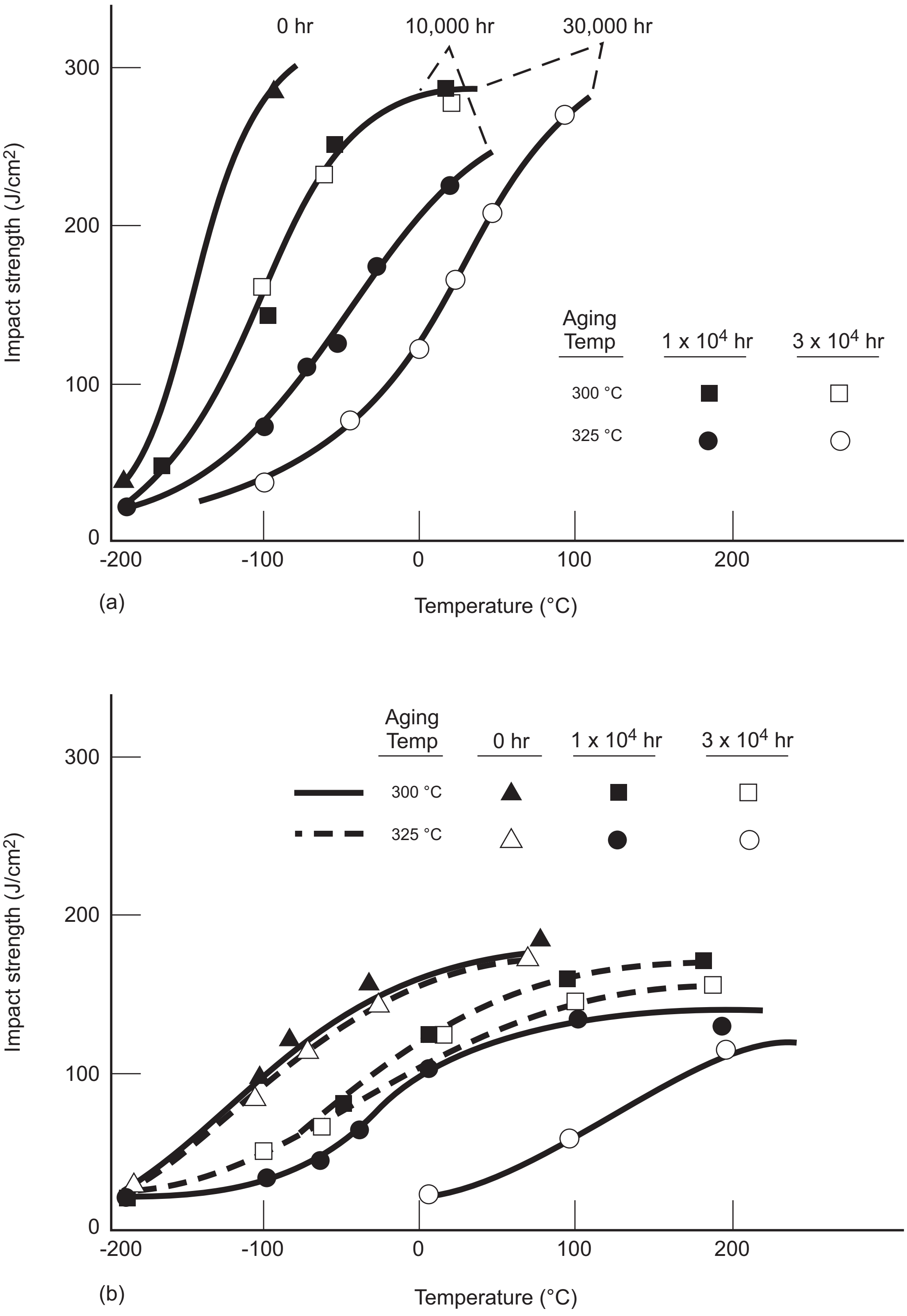
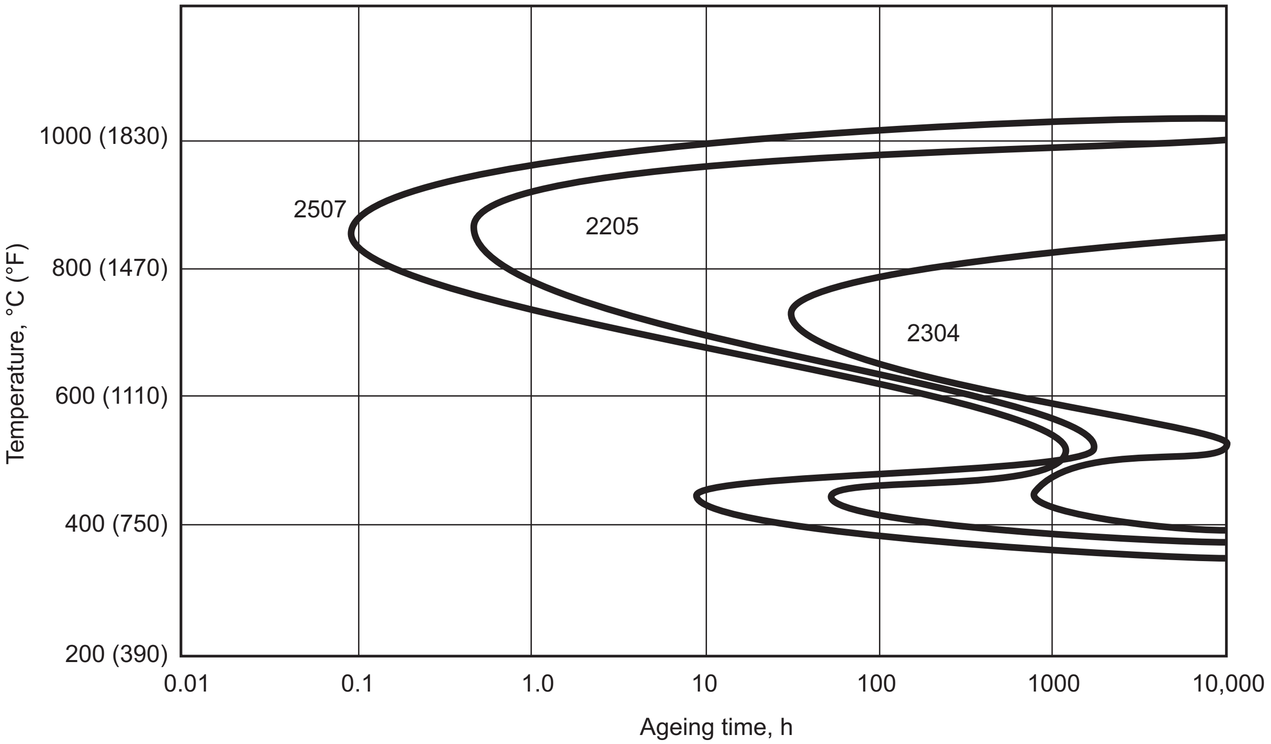


Figure 11—Impact Energy Curves for Alloys Aged at 300 °C or 325 °C: a) Quench Annealed S32750; b) 45 % Cold Worked S31803 [2] [°C = (°F – 32)/1.8]



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

Figure 12—Embrittlement of UNS S32304, S32205, and S32507 after Long Time Annealing [16]

6 Material Specifications

Most users of DSS 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 contains typical added material requirements.

A nitrogen content of 0.14 % minimum in base metals of 22 % Cr DSS is required 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 0.20 % nitrogen. UNS S32205 meets the required nitrogen range (Table 1), but it is not presently in the ASME Code in all product forms. It is believed that this situation will be remedied with time for adoption of revised specifications.

A water quench after final anneal is another common requirement specified to ensure the desired corrosion resistance. This minimizes the time the steel is allowed to be in the 982 °C to 705 °C (1800 °F to 1300 °F) range. ASTM A480 does permit air cooling of sheet when the sheet is processed in a continuous anneal and pickle line, but this method of cooling sheet is very fast. Simple air cooling will not yield the optimal condition for plate of even moderate thicknesses. 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.

To avoid possible detrimental effects of intermetallic precipitates, most refiners' purchase specifications call for a test to indicate their content. If it is unacceptably high, it will affect both low-temperature toughness and corrosion resistance in most aqueous services. The tests typically used are ASTM A923 Test Method B [Charpy V-Notch toughness testing at –40 °C (–40 °F) for standard duplex SS] or Test Method C (ferric chloride corrosion testing). The former test is done not to show adequate toughness for service (although this is also achieved and meets any requirements for toughness testing per Code), 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 criterion of toughness at –40 °C (–40 °F) was selected because it reliably correlated with the presence of intermetallic phases. The impact energy required at this temperature will vary depending on the shelf energy of the annealed base metal.

Tubing is treated differently. 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. Test Method C is also frequently required for tubing. ASTM A923 was originally developed for plate material, but is now commonly applied by users of DSS to other product forms, and to weld procedure qualifications with appropriate adjustments in acceptance criteria.

ASTM A923 contains Test Method B criteria for UNS S31803 and S32205 base metal, HAZs and weld metal, and for 25 % Cr alloy UNS S32750, it states that “the minimum impact energy shall be agreed upon by seller and purchaser.” Some suggested limits 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, S32205, S32750, S32550, and S32520. It is expected that other grades will be added, but the test method can be applied subject to agreement on the test temperature and acceptance criterion.[27]

Many users allow either seamless or longitudinally welded tubing and piping. If welded tubing is allowed, the users typically require that both an electric (eddy current) test and a hydrotest (the ASME material specifications contain both tests, but only one is required) are done. 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 for the base metals.

7 Fabrication Requirements

7.1 Typical Specification Requirements

In addition to special requirements on the materials, special fabrication requirements are also needed to ensure proper corrosion and environmental cracking resistance. These restrictions are applied in addition to the applicable Code requirements, and some of these requirements are given in API 582. The goal of these additional restrictions is to ensure that the fabrication procedures will not significantly diminish the most important engineering properties, namely the corrosion resistance and the mechanical strength/toughness of the steel. Annex B and Annex C show examples of specifications. Typical user specifications add requirements on the topics listed in 7.1.1 through 7.1.4.

7.1.1 Welding

The following are typical specification requirements for welding:

a) cutting and joint preparation restrictions,

b) welding process restrictions,

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

d) the maximum and minimum heat input,

e) a maximum interpass temperature,

f) require GTAW for single-sided welds (with filler metal except for thin gauge material),

g) the backing and shielding gas compositions,

h) require heat tint removal on process side,

i) require removal of arc strikes.

7.1.2 Welding Procedure Qualification (WPS/PQR)

The following are typical specification requirements for WPS/PQR.

a) Added essential variables for each process.

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

   1) ASTM A923 Test Method B and/or Test Method C;

   2) microstructure and percent ferrite from point count;

   3) hardness survey;

   4) for 25 % Cr alloys, ASTM A923 Method C corrosion test (with agreed to criteria).

c) Critical repair welds should be qualified with a partial penetration joint detail and consideration of cumulative heat implications.

7.1.3 Tube-to-tubesheet Joints

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

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

b) other users: allow rolled joints with prequalification mockup tests, including hardness testing;

c) if welding, require mockup and other tests in WPS/PQR.

7.1.4 NDE of Production Welds

The following are typical specification requirements for NDE of production welds:

a) require PT of backgouging;

b) require PT of completed welds;

c) require percent ferrite check, with ferritescope and calibration to AWS A4.2;

d) code-required NDE

7.2 Dissimilar Metal Welding

For dissimilar metal welding, it is generally possible to weld DSS to carbon steel, alloy steels, austenitic SS, and other grades of DSS. The important issues 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 assure a mechanically tough weld. A duplex filler metal is generally used for welded joints between DSS and CS or austenitic SS, but austenitic SS filler metals have also given satisfactory results. Examples of these DSS filler metals are indicated for 22 % Cr and 25 % Cr DSS in Table C.1. Manufacturer's recommendations are typically followed when welding DSS to other alloys, along with the recommendations in API 582.

When welding DSS 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 DSS. 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. This can achieve better corrosion resistance or better weldment properties for thick welds or difficult geometries. 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 have been used successfully, such as ENiCrMo-4, ENiCrMo-10, ENiCrMo-13, and ENiCrMo-14.

7.3 Cold Working, and Hot, and Cold Bending

Solution annealing is generally required by Code or purchaser specification after cold work exceeds 10% deformation for 22 % Cr DSS and on all cold worked or bent (hot or cold) components of 25 % Cr DSS (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 DSS.

Heat exchanger U-bends are difficult to heat treat without some zone of the tubes being exposed to an unacceptable temperature zone 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 DSS 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. [24]

Hot bending is generally done using the induction bending process and prequalified with 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 receive 100 % PT. Dimensional and hardness testing are also performed.

7.4 Hydrostatic Testing

Some specifications limit the chloride content of hydrotest water to 50 ppm to minimize the risk of chloride pitting or SCC during startup, but 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.

Particular attention is also given to drying of the equipment after hydrostatic testing in order to minimize risk of microbiologically influenced corrosion (MIC).

7.5 Tube-to-tubesheet Joints

These joints can be prone to high hardness in welds (due to rapid cooling) and/or in rolls due to the cold work. This is a concern, since DSS air coolers in refining are primarily in relatively severe wet sour services where high hardness (>320 HV) is 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 has been used. Rolled joints can be used with less precaution for other services (e.g. most cooling water and hydrocarbons). In some cases, removal of the crevice to prevent corrosion from the shell-side service (if aqueous) may be needed. When the shell-side service is seawater, some exchangers have been fabricated with crevice free backface welding techniques that involves seal welding of the tubes on the backside of the tubesheet.

7.6 NDE Methods

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

8 Examples of DSS Applications within Refineries

Numerous data sources were reviewed to compile a list of past uses of DSS within refineries. One source that provided many case histories was NACE International's Refin-Cor database. Refin-Cor is a compilation of approximately 45 years of meeting minutes from the Refining Industry Corrosion Group. Table 6 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 7 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 are shown in Table 8. 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 6. Failures could occur in almost all services if improper material quality or fabrication procedures are used.

Table 6—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
08C4.9-11	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 allowing heat treatment of DSS 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 DSS tubes was found to be cost comparable to brass and readily available
08C4.9-11	Cooling Water	Critical bundles in fresh water CW service	2205	None	Replacing CS bundles that were not lasting for two runs
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
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	DSS	None	Replaced Monel, which corroded due to evaporating sour water and deposited salts

Table 6—Case Histories of DSS Uses Reported in NACE International Refin-Cor (Continued)

Item No.	Unit	Service	Grade	Problems	Comments
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
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
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)

Table 6—Case Histories of DSS Uses Reported in NACE International Refin-Cor (Continued)

Item No.	Unit	Service	Grade	Problems	Comments
00F5.8-12	HDS	REAC outlet piping	2205	None	Replaced corroded CS. NH4HS 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
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

Table 6—Case Histories of DSS Uses Reported in NACE International Refin-Cor (Continued)

Item No.	Unit	Service	Grade	Problems	Comments
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 7—Case Histories of DSS 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-side 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

Table 7—Case Histories of DSS 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-side Temp. In/Out (°F)	Tube Pressure (psi)	Comments
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
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
Hydrocracker	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_20, 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

Table 7—Case Histories of DSS 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-side Temp. In/Out (°F)	Tube Pressure (psi)	Comments
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
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
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 DSS looked good.

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

Table 8—Summary List of DSS Refinery Applications to Date

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

Annex A
(informative)

Example of Special Material Requirements for DSS

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

A.1.1 Standard DSS with approximately 22 % Cr shall be specified as UNS S32205 or as dual certified UNS S31803/S32205. DSS with approximately 25 % Cr shall be specified as UNS S31260, S32520, S32550, S32750, S32760, S39274, S39277 or equivalent. When specified by purchaser, super DSS 25 % Cr grades shall have a minimum PREN of 40. Lean DSS shall be specified as UNS S32304, S32101, or S32003.

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

A.1.3 Materials shall be water quenched after the final anneal.

A.1.4 To ensure adequate corrosion resistance, each heat of material of standard DSS grades (except for tubing) 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 25 % Cr grades, both Test Method B and Test Method C shall be done. Test Method B for 25 % Cr 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 25 % Cr grades shall include testing at 40 °C (104 °F) and shall meet 10 mdd maximum. ASTM A923 Method C corrosion test is not appropriate for lean DSS.

A.1.5 Marking materials shall be suitable for SS and contain less than 200 ppm halogens and 200 ppm sulfur. When requested, composition certificates of marking materials shall be provided. Dye stamping of final products is prohibited.

A.1.6 Code required impact testing shall also be met.

A.2 Tubing

A.2.1 Tubing shall be seamless or welded tubing, and if welded tubing is approved, it 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 subsequently VOD or AOD. Secondary melting processes such as VAR and ESR are permitted.

A.2.2 Tubing shall be solution annealed at the minimum temperature or 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 the purchaser.

A.2.3 The hardness testing criteria given in ASME SA-789 shall be modified to Rockwell C 28 maximum for lean and standard 22 % Cr DSS. 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.

A.2.4 For standard 22 % Cr and 25 % Cr DSS, 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. In addition, ASTM A923 Test Method C shall also be done and meet the given criteria, or if not given, then a criteria agreed to by purchaser and supplier.

A.2.5 No weld repairs to tubes are permitted.

A.2.6 Tubes and tube bends shall not be heat treated after bending or straightening. For standard grades, cold work shall be limited to 15 % maximum which is equivalent to limiting U-bending to 3.3D bend radii minimum. For 25 % Cr DSS grades, bends can be made down to 1.5D bend radii with no heat treatment required. If the hardness requirement given in A.2.3 is exceeded doing to working or bending, re-solution annealing per A.2.2 will be required.

A.2.7 Lubricants shall be removed from tube surfaces prior to heat treatment. The fabricator shall submit heat treatment plans for approval, which will include precautions to minimize 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.

A.2.8 After 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 DSS

B.1 The WPS/PQRs shall be qualified in accordance with ASME Section IX and the requirements of this specification. Existing WPS/PQRs, or parts of existing WPS/PQRs may be acceptable provided all of the requirements are satisfied below.

B.2 Each WPS shall contain the information required by ASME Section IX, QW-250, and the following:

a) the specific welding process or combination of processes to be used in production;

b) for filler metal(s), the specific manufacturer(s) and trade name(s) to be used in production as qualified in B4.1.c;

c) details of tack welding technique (where applicable);

d) electrical characteristics of welding [i.e. current and voltage range and polarity for each size (diameter) of filler metal];

e) heat input range;

f) welding head travel speed;

g) maximum interpass temperature.

B.3 For repair welding, details of technique for removing and verifying removal of defects shall be supplied to purchaser for approval before any repairs are done.

B.4 Essential variables for procedure qualification shall be in accordance with ASME Section IX, QW-250, including supplementary essential variables for notch toughness, and those listed below. Any changes in the essential variables of an approved WPS shall require re-qualification.

B.4.1 For manual, semi-automatic and machine welding:

a) **thickness**: In addition to ASME Section IX requirements given in QW-403.6, the maximum qualified thickness shall not exceed 1.2*T*, except for weld coupons of 38 mm (1.5 in.) to 85 mm (3.3 in.), the maximum qualified thickness is 100 mm (4 in.)

b) **joint design**: A change from single to double side welding or vice versa.

c) **filler metal type**: Any change in manufacturer from those used in the procedure qualification or beyond those approved by the purchaser.

d) **filler metal size**: Any change in diameter of the filler metal.

e) **shielding gas flow rate**: Any change in flow rate beyond –20 % to +10 %.

f) **backing gas composition**: Any change in the gas composition.

g) **electrical characteristics**: Any change in type of current, polarity, or pulse range.

h) **interpass temperature**: Any increase in the maximum interpass temperature.

i) **heat input**: Any change greater than ±10 %. Additionally, for single-sided, complete joint penetration welds, the WPS shall restrict the heat input during welding for the root pass and hot pass layers to the PQR heat input values used for these specific layers to ±10 %.

B.4.2 For machine welding only:

a) **joint configuration**: any change in joint configuration outside tolerances specified in the procedure;

b) **weld orientation**: any change in the weld orientation (e.g. vertical to horizontal);

c) **filler metal**: for SAW, any change in the brand name and type of flux.

B.5 Test Quantities

The minimum number of mechanical test specimens required for a welding procedure qualification test weld shall be in accordance with ASME Section IX and Table B.1.

Table B.1—Additional Specimens for PQR Test Weld

Test	Quantity of Specimens
ASTM A923 Test Method B or Test Method C with:	
Test Method B: Charpy V-notch:	
Weld centerline	2
Fusion line	2
Fusion line + 2.5 mm	2
Fusion line + 4.75 mm	2
or	
Test Method C: Ferric Chloride Corrosion Test	2
Cross section for macro-examination, photo-micrographs and ferrite measurements	1
Transverse Hardness Test Surveys	2

B.6 Test Methods

Test procedures and acceptance standards for supplementary welding procedure qualification tests shall be as follows.

B.6.1 ASTM A923 Tests

Charpy impact testing shall be in accordance with ASTM A923 Test Method B, with test results reported. The number of specimens shall be increased in accordance with B.5. Specimens shall be removed from the locations specified by ASME Section IX. Lateral expansion measurements shall be reported for information. Test parameters and criteria shall also be in accordance with A.1.4.

Ferric chloride corrosion tests shall be in accordance with ASTM A923 Test Method C with test results reported. The test specimens shall include weld HAZ and base metal. Test parameters and criteria shall also be in accordance with A.1.4.

The rapid screening test (ASTM A923 Test Method A) shall not be used to approve procedures.

B.6.2 Ferrite Tests (Modified ASTM E562)

B.6.2.1 For ferrite assessment during procedure qualification tests, metallurgical sections shall be polished and etched to clearly reveal the two-phase austenite/ferrite microstructure. The area being point counted, either parent material, weld metal or HAZ, should be examined and photographed under a microscope at a sufficient magnification to fill the field of view and to be able to clearly discriminate between the constituent phases. (For parent plate and weld metal, a magnification of approximately X400 is required, and for HAZ, about X700 to X1000 is recommended.)

B.6.2.2 The photographs shall be overlaid with a grid of at least 100 points and the percentage ferrite shall be calculated from the number of points that fall on the ferrite phase and the total number of points used. Automated counting methods using quantitative metallography equipment can also be used.

B.6.2.3 The ferrite content shall be measured on one of the metallurgical sections using the point counting technique at the following locations:

a) in the parent metal, one measurement on each side of the weld at mid thickness (total of two);

b) in the HAZ on each side of the weld, in the region of the root pass (total of two);

c) in the weld metal, three measurements near to the vertical center line of the weld, one in the cap, one in the root, and one at mid thickness (total of three).

B.6.2.4 Ferrite content limits shall be:

— in the base metal, 30 % to 65 %;

— in the HAZ, 40 % to 65 %; and

— in the weld deposit, 25 % to 60 %.

In less severe services, the purchaser may allow up to 70 %.

B.6.2.5 Experience within the refining industry indicates that this is a difficult test (especially on HAZ) and results are often not accurate. Experienced laboratories should be used.

B.6.3 Photo-micrographs and Macro-examination

B.6.3.1 Photo-micrographs at approximately 400X shall be provided to the purchaser for each of the locations where a phase balance assessment is performed.

B.6.3.2 Photo-micrographs shall show a typical austenite/ferrite microstructure.

B.6.3.3 The macro-examination shall provide evidence that the weld is sound and free from cracks and other defects with full penetration and fusion between weld passes and parent metal.

B.6.4 Hardness Testing

Hardness testing is required on all weld procedure qualification records. Hardness readings shall be taken in Vickers with a 10 kg load (or lighter) for base and weld metal testing and 5 kg load for HAZ testing. At least eight readings at a depth of 2.5 mm below the inside and below the outside surfaces shall be recorded for both base metals, HAZ and weld deposit. Hardness shall not be above 310 HV average, with no reading over 320 HV for standard DSS grades. For other grades, the limit shall be 340 HV average, with no reading over 350 HV.

B.7 Dissimilar Metal Welds

Dissimilar metal welds (i.e. carbon steel to DSS or austenitic SS to DSS) shall require qualification and testing to the requirements of this specification except that the weldment shall not be subjected to ASTM A923 corrosion testing and the non-duplex HAZ need not be subjected to ASTM A923 Charpy testing.

B.8 Third-party Testing

Third-party laboratories used for testing (for both procedure qualifications and production) shall be experienced in the methods used for DSS testing. When requested, the vendor shall submit to the purchaser, the laboratory name and qualifications.

B.9 Tube-to-tubesheet Joints Procedure Qualification Requirements

B.9.1 Tube-to-tubesheet Welded Joints

B.9.1.1 Tube-to-tubesheet welding procedures shall be qualified using a qualification test in accordance with ASME Section IX, QW-193 and the following requirements.

B.9.1.2 The test assembly shall simulate all steps of the production joint including both rolling and welding. In addition, if production welding is to be performed through the plug sheet, this should be simulated in the test assembly (access hole diameter and distance from hole to tubesheet shall be equal to production distances ±10 %).

B.9.1.3 In addition to the macro-examination required by ASME Section IX, QW-193, the microstructure and ferrite content of one randomly selected weld section shall be assessed using the procedures detailed in B6.2 and B6.3.

B.9.1.4 Hardness (HV_{10}) readings shall be taken in the weld deposit and tubesheet base metal, and HV_5 readings shall be taken in the HAZ. A minimum of 6 readings shall be taken on each of the tube-to-tubesheet joints prepared for metallography. Hardness shall not be above 310 HV average, with no readings above 320 HV on standard DSS grades or 340 HV with no readings above 350 HV for other grades.

B.9.1.5 For standard and 25 % Cr grades, a quadrant section of a tube-to-tubesheet weld shall be subject to corrosion testing in accordance with B.6.1.2. No pitting is allowed.

B.9.2 Tube-to-Tubesheet Rolled Joints

Rolling shall be prequalified by a mock up and hardness testing. The mockup test assembly shall as described in ASME Section IX, QW-193 with a minimum of ten rolled-in tube samples but without welding. The rolling procedure should be the same as the procedure that will be used during production. Hardness readings shall be taken in Vickers with a 10 kg load. At least eight readings shall be recorded. Hardness values shall not exceed the limits given in B.9.1.4. Rolled surfaces shall not extend past the tubesheet or into weld areas.

B.9.3 Tube-to-tubesheet Rolled and Welded Joints

Rolled and welded joints shall be prequalified in accordance with B.9.1 and B.9.2.

Annex C
(informative)

Example of Special Welding and Fabrication Requirements for DSS

C.1 Joint Preparation

C.1.1 DSS may be cut using the plasma-arc process, a machine cutter, or grinding disc dedicated solely for the use on DSS. Carbon-arc shall not be used for cutting or back-gouging. If plasma-arc cutting is used, the inside surface must be thoroughly cleaned of all spatter. Sufficient metal shall be removed in the beveling process to remove any HAZ that occurred as a result of the plasma-arc cutting. Once used for cutting DSS, grinding discs shall be used exclusively for that purpose, and contamination with carbon steel should be avoided during all steps. The final surface preparation and configuration shall be obtained by machining. During machining operations, only a cutting fluid compatible with SS shall be used.

C.1.2 Any small burrs, nicks, or other irregularities on the weld bevel shall be repaired, if possible, by light grinding. Any suspected edge defects or laminations shall be reported to the purchaser prior to proceeding with investigation or repairs. Repairs by welding shall not proceed without prior approval of the purchaser.

C.1.3 Each beveled edge, and internal and external surfaces over a distance of at least 50 mm (2 in.) back from the bevel shall, immediately prior to welding, be thoroughly dried, and shall be cleaned with an SS wire brush. The beveled edge shall then be wiped clean with acetone, or other purchaser-approved solvent.

C.2 General Welding Requirements

C.2.1 All production welds, including tack welds and tube-to-tubesheet welds, shall be made with filler metal. Autogeneous welding (without filler metal) is not permitted. The following consumables shall be used unless otherwise authorized by the purchaser.

Table C.1—Welding Consumables

Process	22 % Cr	25 % Cr (Note 1)
SMAW	SFA 5.4 E2209	SFA 5.4 E2594
GTAW/GMAW	SFA 5.9 ER2209	SFA 5.9 ER2594
SAW	SFA 5.9 ER2209 with a flux designed for DSS	SFA 5.9 ER2594 with a flux designed for DSS
NOTE 1 This table does not cover some of the 25 % Cr alloys with additional alloying elements such as tungsten or copper. The material manufacturer's recommendations on welding consumables shall be followed.		

The fabricator may propose 25 % Cr filler materials for 22 % Cr base metals to the purchaser for approval, especially if needed to pass corrosion resistance testing.

Plasma arc welding may also be used with purchaser approval.

C.2.2 Maximum and minimum heat inputs shall not exceed the values qualified in accordance with B.4.1 h), with no value exceeding 2.5 kJ/mm or being below 0.5 kJ/mm for standard DSS alloys. Heat input for tube-to-tubesheet welding may be as high as 3.5 kJ/mm, assuming that when the ferrite is checked during the procedure qualification, it is found to be within the limits specified for the weld deposit and HAZ.

Tighter limits may be recommended by the filler metal manufacturer, especially for thinner welds, weld type, welding process, base metal chemistry, etc. Limits for all DSS alloys shall be based on the manufacturers' recommendations.

C.2.3 The maximum interpass temperature shall not exceed the value qualified in accordance with B.4.1 g) and this temperature shall not exceed 150 °C (300 °F) for standard and lean DSS alloys and 120 °C (250 °F) for 25 % Cr alloys. Measurements shall be taken on the parent metal surface, directly adjacent to the weld groove, using a contact thermometer with an instant digital display. Temperature-indicating crayons can be used with purchaser approval. If the crayons are used, certificates from the crayon manufacturer shall be available for review by the purchaser's representative, which certify a maximum halogen content of 200 ppm and maximum sulfur content of 200 ppm.

C.2.4 All single-sided welds shall be made with a GTAW root pass and back purged until at least $^1/_4$ in. (6 mm) of weld metal thickness has been deposited. Backing gas shall be welding grade 90 % nitrogen/10 % hydrogen mixture, pure nitrogen or argon/nitrogen mixture with not less than 5 % nitrogen. The oxygen content of the back-purged volume shall be less than 0.25 % (2500 ppm). The seller shall submit details of the method and equipment to be used for monitoring oxygen content as part of the WPS. Shielding gasses can be argon or argon with 2 % maximum nitrogen.

C.2.5 Under no circumstances shall the welding arc be struck outside the weld bevels. If this occurs, the arc strike shall be removed by grinding. The ground area shall be examined with liquid penetrant, and any relevant indications will require repairs.

C.2.6 During production welding, calibrated equipment for measuring the following variables shall be available at all times:

a) welding current (amperage);

b) arc voltage;

c) interpass temperatures (digital);

d) oxygen content of backing gas;

e) wire feed speed;

f) travel speed;

g) shielding and backing gas flow rate.

C.2.7 Welds which are backgouged for welding on the opposite side shall have liquid penetrant examination after cleaning for the backweld. All backgouging shall be accomplished with approved procedures, insuring complete removal of oxides from plasma-cut surfaces. Carbon arc gouging shall not be used.

C.2.8 All accessible welds exposed to the process side shall be cleaned after welding by hand wire brushing (with an SS wire brush) on the as-welded surfaces.

C.2.9 All welds made, including tack and fitup, shall be done with approved weld procedures, materials and certified welders.

C.2.10 Weld maps shall be incorporated on drawings submitted with applicable weld procedures, for review and authorization to proceed.

C.3 Tube-to-tubesheet Joints

C.3.1 The general welding requirements of Section 1 and Section 2 shall apply to tube-to-tubesheet welding, as applicable.

C.3.2 Tube-to-tubesheet welds shall be made using either the GTAW or GMAW process with the addition of filler metal. The weld throats (minimum leak paths) shall not be less than the thickness of the tube wall.

C.3.3 Welds shall be made with a shielding gas containing 2 % to 3 % nitrogen.

C.3.4 For strength welded joints, no rolling shall be used, except that a light roll solely to maintain fitup for welding is acceptable (<3 %). Any additional rolling requires approval from the purchaser. Rolled surfaces shall not extend past the tubesheet or into the weld area.

C.3.5 For rolled joints or rolled and welded joints, rolled surfaces shall not extend past the tubesheet or into weld areas.

C.3.6 A fabrication plan shall be submitted for approval, and shall include cleaning prior to assembly, welding and rolling sequences, and inspections as a minimum.

C.4 NDE and Testing in Addition to Applicable Fabrication Codes

C.4.1 PT

All accessible completed production welds shall be PT examined. Procedures and acceptance criteria shall be in accordance with ASME Section VIII, Division 1, Appendix 8. The examination shall include a band of base metal at least one in. wide on each side of the weld and both faces of the joint (if accessible).

C.4.2 Ferrite Checks

The ferrite content of all accessible completed production welds on the weld deposit only shall be checked using a ferritescope. A minimum of three tests shall be made on each 1.5 m (5 ft) of weld. The average value of the ferritescope readings on each weld shall be 25 % to 65 %. For calibrating the ferritescope, the volume percent ferrite shall be determined using a ferritescope at similar locations as those tested using the point counting technique (see B.6.2).

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