Use of Duplex Stainless Steels in the Oil Refining Industry

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Introduction

Duplex stainless steels (DSSs) are finding increasing use in the petroleum refining industry, primarily because they often offer an economical combination of strength and corrosion resistance. These stainless steels (SSs) typically have an annealed structure that is nominally half ferrite and half austenite, although the ratios can vary from ~35/65 to 65/35. Most refinery applications where DSSs are used are corrosive, and DSSs or other higher alloys are required for adequate corrosion resistance. In some refineries, DSSs are being considered as a "baseline" material.[1] In these facilities, DSSs are being used in applications where carbon steel may be acceptable, but DSSs have been shown to be more economical, considering their higher strength and better long-term reliability.

DSSs are often used in lieu of other grades of SS, such as the austenitic, ferritic, and martensitic types, because of their superior properties and corrosion resistance. For example, DSSs provide improved resistance to chloride pitting and chloride stress corrosion cracking in comparison to austenitic SS. Higher alloyed DSSs like super duplex and hyper duplex are an economic alternative to more expensive alloys with similar corrosion resistance. Figure 1 provides a comparison of DSS alloys with various austenitic SS showing the difference in strength and chloride corrosion resistance expressed as pitting resistance equivalent number (PREN), which is defined in 5.1.[2] This chart shows the excellent combinations of higher strength and corrosion resistance available with DSSs. It also shows that there are "subfamilies" of specific grades within both the DSSs and austenitic families. This is also illustrated in Table 1.

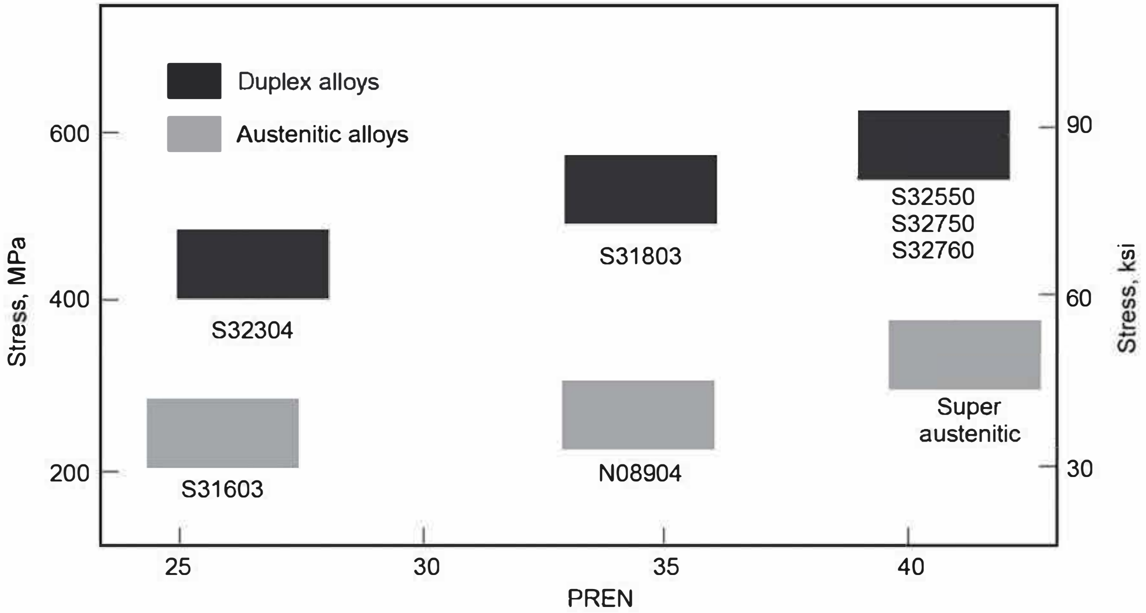


Figure 1—Comparison of the Proof Stress and Pitting Resistance (Based on PREN of the Bulk Chemistry) of Duplex and Austenitic SS [2]

DSSs have existed since the 1930s. However, the first-generation alloys such as Type 329 (UNS S32900) had unacceptable corrosion resistance and toughness in weldments. [3] [4] [5] Hence, the initial applications were almost exclusively limited to heat exchanger tubing, particularly in corrosive cooling water services and shafts or forgings. In the 1980s, second-generation DSSs that had overcome the problems with welds became commercially available. These new grades had nitrogen additions promoting better austenite/ferrite balances at welds and heat-affected zones (HAZs). Additionally, improved DSS welding practices led to improvement in weldment mechanical strength, toughness, and corrosion resistance, achieving values comparable to annealed base metal. DSSs most commonly used in refineries today include those with 22 %, 25 %, and 27 % Cr. The 22 % Cr alloy is the industry workhorse. The 25 % Cr (super duplex grades) and 27 % Cr (hyper duplex grade), containing more molybdenum and nitrogen (having higher PREN values than 22 % Cr duplex steels) are finding more applications. Lean DSS grades are beginning to be accepted in less arduous environments (e.g., cooling water exchangers).

Table 1 lists the compositions and UNS numbers of various common DSSs, including some first generation DSSs for comparison. Note that UNS S32205 is a "newer version" of UNS S31803, and while it also meets the S31803 chemistry, it is produced with a higher minimum nitrogen, chromium, and molybdenum content. In many cases, the material is dual-certified as S31803/S32205 to ensure the corrosion resistance and weldability of 32205 is retained while taking advantage of the higher allowable stress values for 31803. ASME and ASTM standards for duplex SS grades are given in Table 2, while Table 3 provides the mechanical properties. Type 316L and other austenitic SSs are included in these tables for comparison.

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

1) environment-related failure mechanisms associated with DSSs and the preventative measures to avoid them;

2) typical DSS material specification requirements used by refiners;

3) typical DSS fabrication specification requirements used by refiners;

4) examples of applications of DSSs within refineries.

Use of Duplex Stainless Steels in the Oil Refining Industry

1 Scope

This report covers many of the “lean,” “standard,” “super,” and “hyper” grades of duplex stainless steels (DSSs) most commonly used within refineries. These terms have not been firmly established by the industry, and their use may vary between literature references and suppliers. The ISO document ISO 17781 *Petroleum, Petrochemical and Natural Gas Industries—Test Methods for Quality Control of Microstructure of Ferritic/Austenitic (Duplex) Stainless Steels* provides a fairly consistent and inclusive classification of these materials based on their chemical composition and corrosion resistance.

In an attempt to facilitate future cross reference, this document adopted materials classifications consistent with ISO 17781. The following list summarizes the classification group (refer to Table 1 for a complete list of grades):

— Type 20 Cr Duplex, Group A (Lean DSSs): S32001, S32101, S32202, S82011, S82031, and S82441;

— Type 20 Cr Duplex, Group B (Lean DSSs): S32003, S32304, S31500, S81921;

— Type 22 Cr Duplex (Standard DSSs): J92205, S31803, S32205;

— Type 25 Cr Duplex (Super DSSs): S32520, S32550, S32750, S32760, and S32906;

— Type 27 Cr Duplex (Hyper DSSs): S32707, S33207.

Grades that are labeled as “lean” (including grades sometimes called “semi-lean”) have lower Cr, Ni, or Mo than the standard grades and thus a lower PREN, and they are used in some process services that are less aggressive (primarily in corrosive environments to replace 304L SS). These lean DSSs have been used for heat exchanger tubing, storage tanks, and structural applications primarily for their higher strength compared with carbon steel (CS).

Formable duplex stainless steel is a new kind of DSS with improved formability due to the transformation-induced plasticity (TRIP) effect, enabling the manufacture of heavily cold-worked components like tray internals, plate and frame heat exchangers, and twisted tubes, among others. The corrosion resistance of the material in the cold-worked condition is similar to the annealed form.[42]

Product forms within the scope of this report are: tubing, plate, sheet, forgings, castings, hot isostatically pressed (HIP) components, pipe, and fittings for piping, vessel, exchanger, and tank applications. The use of DSSs for tanks is also addressed by API Standard 650. The limited use of DSSs as a cladding is also briefly covered within this document.

The majority of refinery services in which DSSs are currently being used or being considered for use in the petroleum refining industry include:

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

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

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

d) amines, such as:

   1) MEA, MDEA, DEA, etc., or

    2) other environments, such as those containing caustic;

e) low pH waters containing chlorides.

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

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

UNS Number	Type [b]	Mass % [a, e]										
		Cr	Mo	Ni	N	Cu	C	Mn	P	S	Si	Other
Lean DSSs /Type 20 Cr Group A Duplex.[f] 24.0 ≤PREN<28 (consistent with ISO 17781 Annex A)												
S32001	—	19.5–21.5	0.6	1.0–3.0	0.05–0.17	1.0	0.03	4.0–6.0	—	—	—	—
S32101	2101	21.0–22.0	0.10–0.80	1.35–1.70	0.20–0.25	0.10–0.80	0.04	4.0–6.0	0.04	0.03	1.0	—
S32202	2202	21.5–24.0	0.45	1.00–2.80	0.18–0.26	—	0.03	2	0.04	0.01	1.0	—
S82011	2102	20.5–23.5	0.10–1.00	1.0–2.0	0.15–0.27	0.5	0.03	2.00–3.00	0.04	20	1.0	—
S82031 [g]	—	19.0–22.0	0.6–1.4	2.0–4.0	0.14–0.24	—	0.03	2.5	0.04	0.005	0.8	—
S82441	2404	23.0–25.0	1.00–2.00	3.0–4.5	0.20–0.30	0.10–0.80	0.03	2.5–4.0	0.035	0.005	0.7	—
Lean DSSs /Type 20 Cr Group B Duplex.[f] 28.0 ≤PREN<30 (consistent with ISO 17781 Annex A)												
S32003	2003	19.5–22.5	1.50–2.00	3.0–4.0	0.14–0.20	—	0.03	2.0	0.03	0.02	1.0	
S32304	2304 [c]	21.5–24.5	0.05–0.60	3.0–5.5	0.05–0.20	0.05–0.60	0.03	2.5	0.04	0.03	1.0	—
S31500	“3RE60”	18.0–19.0	2.5–3.0	4.25–5.25	0.05–0.10	—	0.03	1.20–2.00	0.03	0.03	1.40–2.00	—
S81921	—	19.0–22.0	1.0–2.0	2.0–4.0	0.14–0.20	—	0.03	2.0–4.0	—	—	—	—
Standard DSSs/Type 22 Cr Duplex,[f] 30.0≤PREN<40 and Cr≥19.5 % (consistent with ISO 17781 Annex A)												
J92205	—	21.0–23.5	2.5–3.5	4.5–6.5	0.10–0.30	1.0	0.03	1.5	—	—	—	—
S31803	—	21.0–23.0	2.5–3.5	4.5–6.5	0.08–0.20	—	0.03	2.0	0.03	0.02	1.0	—
S32205	2205 [c]	22.0–23.0	3.0–3.5	4.5–6.5	0.14–0.20	—	0.03	2.0	0.03	0.02	1.0	—
S31200	—	24.0–26.0	1.2–2.0	5.5–6.5	0.14–0.20	—	0.03	2.0	—	—	—	—
S32404	—	20.5–22.5	2.0–3.0	5.5–8.5	0.20–0.30	1.0–2.0	0.04	2.0	—	—	—	—
S32506	—	24.0–26.0	3.0–3.5	5.5–7.2	0.08–0.20	—	0.03	1.0	—	—	—	W: 0.05 to 3.0
S32808	—	27.0–27.9	0.8–1.2	7.0–8.2	0.30–0.40	—	0.03	1.1	—	—	—	W: 2.1 to 2.5
S32900	Type 329	23.0–28.0	1.0–2.0	2.5–5.0	—	—	0.08	1.0	0.04	0.03	0.75	—
S82011	2102	20.5–23.5	0.10–1.00	1.0–2.0	0.15–0.27	0.5	0.03	2.00–3.00	0.04	0.2	1.0	—
S82122	—	20.5–21.5	0.6	1.5–2.5	0.15–0.20	0.5–1.5	0.03	2.0–4.0	—	—	—	—
S82551	—	24.5–26.5	0.75–2.00	4.5–6.5	0.10–0.35	2.0–3.0	0.03	1.5	—	—	—	—
Super DSSs Type 25 Cr Duplex, 40.0≤PREN<48 (consistent with ISO 17781 Annex A)												
J93404	—	24.0–26.0	4.0–5.0	6.0–8.0	0.10–0.30	—	0.03	1.5	—	—	—	—
J93380	—	24.0–26.0	3.0–4.0	6.5–8.5	0.20–0.30	0.5–1.0	0.03	1.0	—	—	—	W: 0.5 to 1.0
S31260	—	24.0–26.0	2.5–3.5	5.5–7.5	0.10–0.30	0.2–0.8	0.03	1.0	0.035	0.02	0.8	W: 0.1 to 0.5
S32520	—	24.0–26.0	3.0–5.0	5.5–8.0	0.20–0.35	0.50–3.00	0.03	1.5	0.035	0.02	0.8	—

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

Mass % [a, e]												
UNS Number	Type [b]	Cr	Mo	Ni	N	Cu	C	Mn	P	S	Si	Other
S32505	—	24.0–27.0	2.9–3.9	4.5–7.0	0.25–0.30	1.5–2.5	0.03	1.5	0.035	0.02	0.8	—
S32550	255 c	24.0–27.0	2.9–3.9	4.5–6.5	0.10–0.25	1.50–2.50	0.04	1.5	0.04	0.03	1.0	—
S32750	2507 c	24.0–26.0	3.0–5.0	6.0–8.0	0.24–0.32	0.5	0.03	1.2	0.035	0.02	0.8	—
S32760 [d]	“Z100”	24.0–26.0	3.0–4.0	6.0–8.0	0.20–0.30	0.50–1.00	0.03	1	0.03	0.01	1.0	W: 0.5 to 1.0
S32906	—	28.0–30.0	1.50–2.60	5.8–7.5	0.30–0.40	0.8	0.03	0.80–1.50	0.03	0.03	0.8	—
S32950	—	26.0–29.0	1.0–2.5	3.5–5.2	0.15–0.35	—	0.03	2	0.03	0.03	0.8	—
S39274	—	24.0–26.0	3.0–4.0	6.5–8.0	0.23–0.33	1.2–2.0	0.025	—	0.03	0.03	0.8	W: 0.8 to 1.2
S83071	—	29.0–31.0	3.0–4.0	6.0–8.0	0.28–0.40	0.80	0.030	0.5–1.5	0.030	0.020	0.50	—
Hyper DSSs Type 27 Cr Duplex, 48.0≤PREN<55 and Chrome < 33.0 % (consistent with ISO 17781 Annex A)												
S32707	2707 [c]	26.0–29.0	4.0–5.0	5.5–9.5	0.30–0.50	1	0.03	1.5	0.035	0.01	—	Co:0.5 to 2.0
S33207	3207 [c]	29.0–33.0	3.0–5.0	6.0–9.0	0.40–0.60	1	0.03	1.5	0.035	0.01	—	—
Austenitic SS												
S31603	Type 316L	16.0–18.0	2.0–3.0	10.0–14.0	0.1	—	0.03	2	0.045	0.03	0.75	—
S31703	Type 317L	18.0–20.0	3.0–4.0	11.0–15.0	0.1	—	0.03	2	0.045	0.03	0.75	—
N08020	“Alloy 20”	19.0–21.0	2.0–3.0	32.0–38.0	—	3.00–4.00	0.07	2	0.045	0.035	1.0	Cb + Ta: 8 × C–1.00
N08904	904L	19.0–23.0	4.0–5.0	23.0–28.0	0.1	1.00–2.00	0.02	2	0.04	0.03	1.0	—
N08028	Alloy 28	26.0–28.0	3.0–4.0	30.0–34.0	—	0.60–1.40	0.03	2.5	0.03	0.03	1.0	—

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

Mass % [a, e]												
UNS Number	Type [b]	Cr	Mo	Ni	N	Cu	C	Mn	P	S	Si	Other
6 % Mo Super Austenitic SS												
N08367	—	20.0–22.0	6.0–7.0	23.5–25.5	0.18–0.25	0.75	0.03	2	0.04	0.03	1.0	—
S31254	—	19.5–20.5	6.0–6.5	17.5–18.5	0.18–0.22	0.50–1.00	0.02	1	0.03	0.01	0.8	—
N08926	—	19.0–21.0	6.0–7.0	24.0–26.0	0.15–0.25	0.50–1.50	0.02	2	0.03	0.01	0.5	—

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

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

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

[d] Minimum PREN (see equations in 5.1) is calculated based on the minimum chemistry requirements based on the overall alloy chemistry—see footnote f. Note that UNS S32760 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.

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

[g] Formable duplex N82031 not yet categorized by ISO 17781.

Table 2—ASME, ASTM, and ISO Specifications for DSSs

Product Form	ASME or ASTM Specifications
Plate, Sheet	SA-240, SA-480
Bar Products	SA-479, A276
Pipe	SA-790, A928
Tubing	SA-789
Fittings	SA-815
Forgings	SA-182
Castings	SA-351, A890, A995
HIP products	ASTM A988
Bolting	ASTM A1082
Testing	2—ASME, ASTM, and ISO Specifications for DSSs

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

UNS Number	Type	Tensile Strength, min		Yield Strength, min		Elongation min %	Hardness, max	
		MPa	ksi	MPa	ksi		Brinell	Rockwell C
S32304	2304	600	87	400	58	25.0	290	—
S32101	2101	650	95	450	65	30.0	290	—
S32202	2202	650	94	450	65	30.0	290	—
S32003	2003	620	90	450	65	25.0	293	31
S82011 (>5 mm)	2102	655	95	450	65	30	293	31
S82441 (≥10 mm)	2404	680	99	480	70	25	290	—
S82031	—	700	101.5	500	72.5	35	290	—
S31803	—	620	90	450	65	25.0	293	31
S32205	2205	655	95	450	65	25.0	293	31
S32550	255	760	110	550	80	15.0	302	32
S32750	2507	795	116	550	80	15.0	310	32
S32760	Z100	750	108	550	80	25.0	270	—
S32906 (≥4 mm)	—	750	109	550	80	25.0	310	32
S32707[a]	2707	920	133	700	101	25	318	34
S31603	316L	485	70	170	25	40.0	217	95 R_b [c]
N08825[b]	825	586	85	241	35	30.0	—	—

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

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

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

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

2 Normative References

There are no normative references in this document.

3 Terms, Definitions, Acronyms, and Abbreviations

3.1 Terms and Definitions

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

3.1.1

duplex stainless steel (DSS)

Stainless steels with ~50 % austenitic and 50 % ferritic microstructure.

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, that while not melted, has been microstructurally affected by the heat of welding. This zone typically has high residual welding stresses, unless solution annealing is performed and the stresses can extend beyond the HAZ. For modern DSSs, the transformed zone is typically a maximum of 0.5 mm (0.02 in.) wide when proper weld procedures are used.

3.1.3

naphthenic acid

Organic molecules with carboxylic functional units that are present in certain crude oils and distillate streams in a crude distillation unit and can cause corrosion at temperatures > 232 °C (450 °F).

3.1.4

weld

The localized coalescence of metal composed of either melted filler metal diluted with some melted base metal or solely melted base metal (autogenous).

3.1.5

weldment

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

3.2 Acronyms

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

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

4 Metallurgy of Duplex Stainless Steels (DSSs)

4.1 Background

To achieve proper material specification, fabrication, and welding practices, it is necessary to have an understanding of the metallurgical structure of DSS and the effect that various treatment and fabrication practices might have on the toughness and corrosion resistance of these alloys. Therefore, the metallurgy of DSSs is one of the first topics covered in this report. The subsequent discussion covers the resistance of DSSs to specific degradation mechanisms and generally assumes properly produced and fabricated base materials and welds unless otherwise indicated.

Both the early and current grades of DSSs, in the annealed condition, have good localized corrosion resistance because of their high chromium and molybdenum content. However, when the first generation duplex grades were welded, they lost the optimal phase balance and were prone to the precipitation of intermetallic phases in the weld and heat-affected zone (HAZ) resulting in weldments with poor corrosion resistance and toughness. This problem was overcome in the 1980s by the addition of nitrogen, an inexpensive austenite-former, which achieved a superior austenite-ferrite balance. The addition of nitrogen also resulted in other benefits, including retarded sigma phase precipitation, improved toughness, higher tensile and yield strength, and improved pitting and crevice corrosion resistance. Close attention to the welding procedure is still necessary to obtain the optimum results, as poor welding practices could result in the precipitation of chrome nitrides.

Although there are many secondary phases that can form during the metal solidification, heat treatment, or prolonged high-temperature exposure in service, the three common detrimental phases are:

- alpha prime (α')—alpha prime is normally formed while in service and it is the cause of 475 °C (885 °F) embrittlement (see 5.7);
- sigma phase (σ)—sigma phase is formed during slow cooling from heat treatment or welding in the temperature range of 590 °C–980 °C (1100 °F–1800 °F); and
- chromium nitrides (CrN, Cr_2N)—chromium nitrides are formed as a consequence of rapid cooling through the temperature range of 700 °C–900 °C (1290 °F–1650 °F) (see Figures 2 and 3).

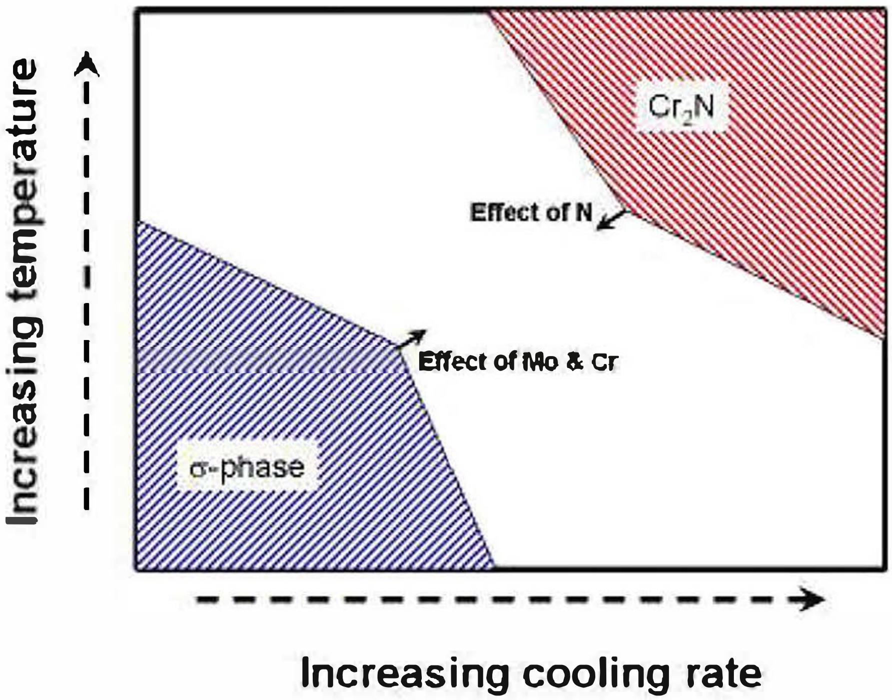


Figure 2—Schematic Diagram Showing the Conditions Under Which σ-Phase and Chromium Nitrides Are Formed in a Space Defined by Temperature and Cooling Rate. [43]

4.2 Solidification

DSSs initially solidify as fully ferritic structures, and upon further cooling, some of the ferrite transforms to islands of discontinuous austenite within the continuous ferritic matrix. Nitrogen raises the austenite formation temperature (see Figure 3) and promotes the timely formation of austenite, enabling the achievement of the desired phase balance, even at relatively rapid cooling rates. This favorable effect occurs during solidification (casting and welding), during annealing, and during other high-temperature exposures (e.g., weld HAZs). Controlled additions of nitrogen reduce the risk of excess ferrite in the HAZ (see 4.3).

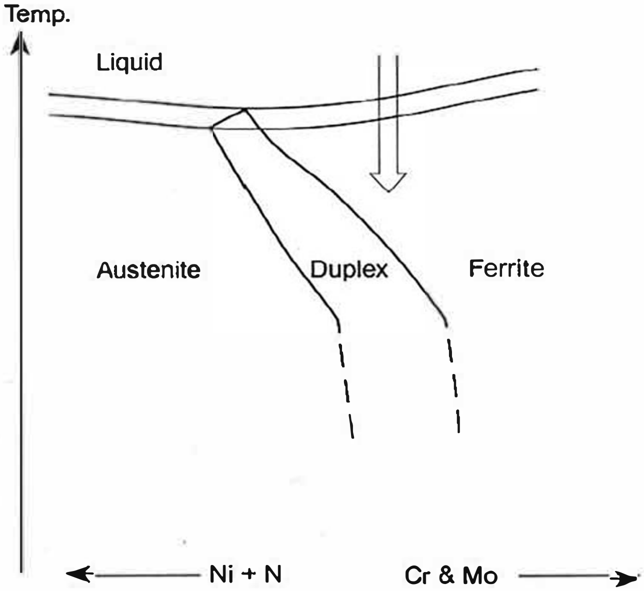


Figure 3—Solidification and Phase Development of Duplex Stainless Steels

In some grades of DSS, the partitioning of alloying elements such as Cr, Ni, N, or Mo can lead to differences in the corrosion resistance between the phases in certain environments. For example, selective austenite attack has occurred on S32205 DSS in certain types of flue gas desulfurization (FGD) units, while other services have had selective ferrite attack. This is discussed further in 5.1 and 5.5. Partitioning depends on both the chemistry and the thermal history.

4.3 Problems to be Avoided During Welding

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

1) excessive ferrite in the HAZ or weld deposit due to rapid cooling or low nitrogen content;

2) precipitation of chromium nitrides due to rapid cooling;

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

Rapid quenching after welding is damaging to DSSs if it causes the steel to remain mostly ferritic as it cools from the high temperatures incurred during welding operations. This has been experienced in heavy wall sections where conduction through the workpiece provides the rapid quench. Resistance welds, welds of sheet liners to plates, or tube-to-tubesheet welds and header boxes are examples of situations susceptible to extremely rapid quenching. Addition of nitrogen to the base metal, filler material, and shielding gas (when applicable) promotes rapid austenite formation, making DSSs less sensitive to this problem.

Precipitation of chromium nitrides is associated with super-saturation of nitrogen in the ferrite phase, which occurs due to too low heat input, or due to the heat sink effect during welding of heavy wall components. Precipitation of sigma phase and other harmful intermetallic phases are normally associated to excessive heat input or prolonged exposure to 590 °C–980 °C (1100 °F–1800 °F) temperature range due to multi-pass welding. It can be mitigated by using welding parameters that provide an adequate balance between cooling rates and time at temperature.

The addition of preheat is typically performed with great care to prevent elevated temperature exposure, and temperatures at the weldment should never exceed the maximum recommended interpass temperature for the specific grade. Excessive preheat and interpass temperatures will result in slow cool down rates and increase the risk of sigma phase precipitation.

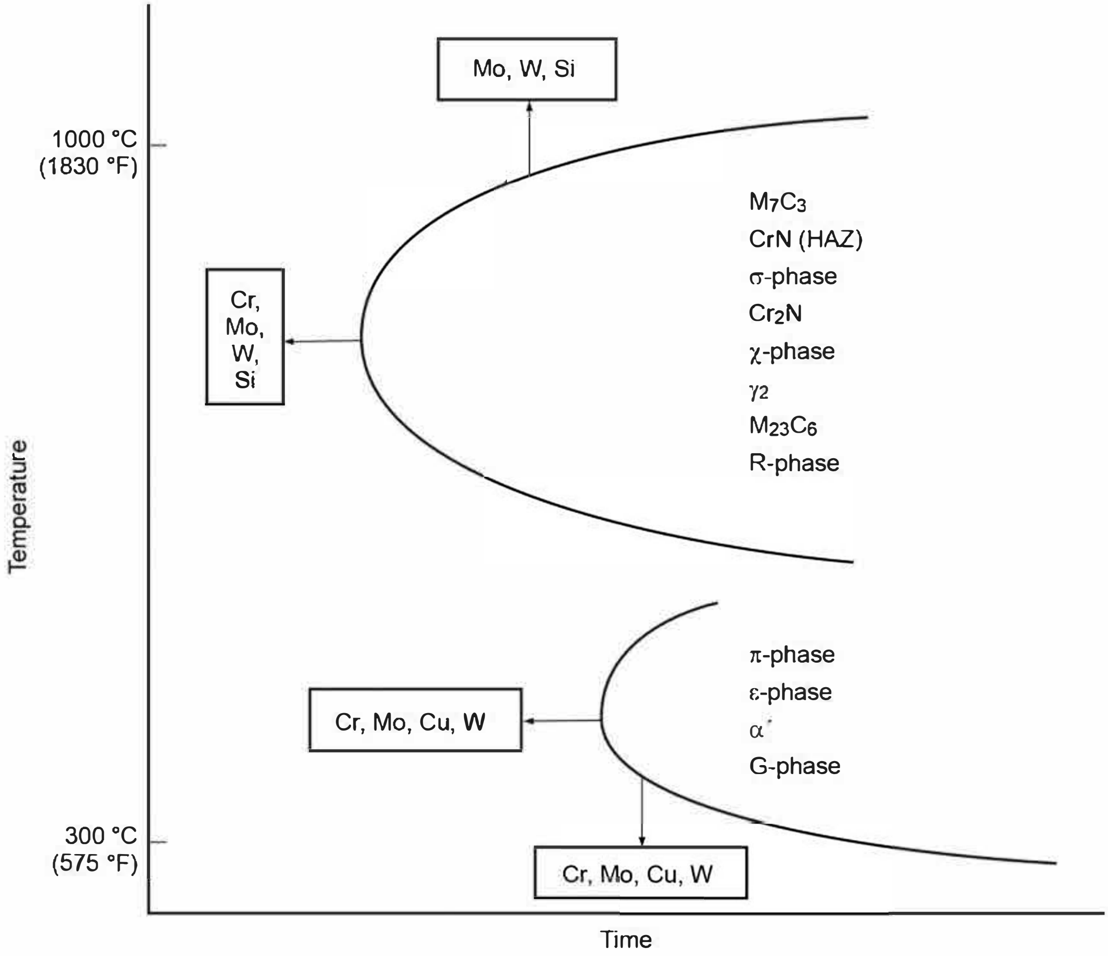
Suggested limits on the ferrite content in weld and HAZ (appropriate for most refinery applications) are given in API Recommended Practice 582 and ISO 17781. However, for particular applications, a tighter ferrite content range may be specified. For example, API Recommended Practice 932-B specifies a tighter ferrite content range for REACs. Mockups are typically required for tube-to-tubesheet welding procedure qualifications to verify that welding parameters will result in the weldment achieving the proper austenite-ferrite phase balance.

The precipitation of harmful intermetallic phases results from excessively high heat inputs during welding or materials exposure to the temperature range of 700 °C to 955 °C (1300 °F to 1750 °F) as shown in Figures 2 and 4. These intermetallic phases are extremely detrimental to impact toughness and corrosion resistance.[4] [5] The rate of this diffusion-controlled precipitation process is most rapid at 815 °C to 870 °C (1500 °F to 1600 °F), and intermetallic phase precipitation is cumulative with each exposure. The cooling time after the final annealing process, hot forming, and all welding (including future repairs) should be included in the evaluation of total exposure times. The descriptive comparisons below and Figure 5 show the total exposure times required for the precipitation of unacceptable amounts of intermetallic phase for three different DSS, and precise values vary by composition and other variables.

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

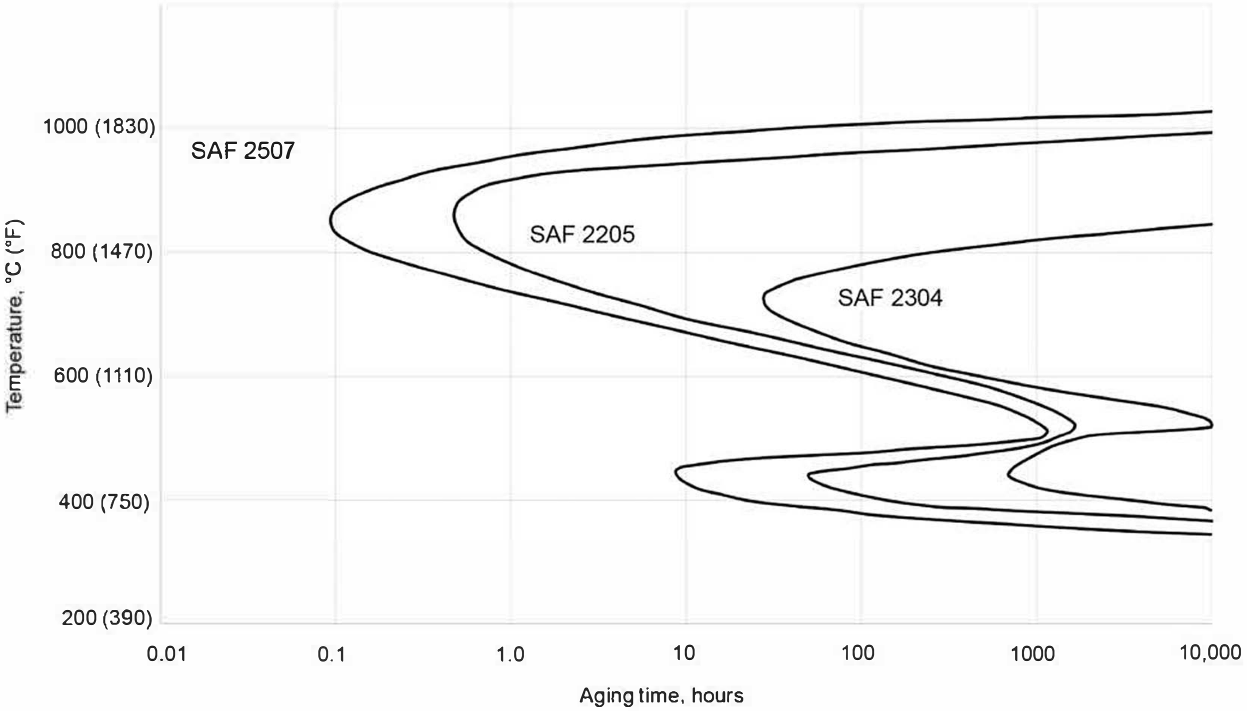
— super and hyper DSSs show similar degradation after shorter exposure times (minutes) at a temperature of 850 °C (1560 °F);

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



NOTE: Similar curves are also shown in Figure 5, which shows the different curves for different grades of DSS.

Figure 4—Possible Precipitation Phases in DSSs [2]



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

Figure 5—Embrittlement by Precipitation of Harmful Phases of UNS S32304, S32205, and S32507 after Long-time Annealing [31]

Because the cooling provided by the work piece itself is very effective in reducing the time the weldment is in the temperature range for intermetallic phase formation, a low interpass temperature during welding is desirable for minimizing the formation of such phases. Typically, the maximum interpass temperature is limited to prevent precipitation of intermetallic phases and control phase balance. Temperature limits vary by chemical composition and thickness. Limitations on interpass temperature are typically imposed when qualifying a welding procedure, and monitoring is done during production welding to assure that the interpass temperature is no higher than that used in the procedure qualification. See API Recommended Practice 582 for specific welding details for DSSs.

Once intermetallic phases precipitate, they can only be eliminated by a full solution anneal process, followed by rapid cooling to prevent reformation. Performing such treatment may not be possible on a large fabricated component, like piping modules, pressure vessels, or tanks. In that case, it would be necessary to cut out the affected region and make a qualified repair.

4.4 Low- and High-temperature Properties

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

Toughness of DSS welds varies due to the differences in the amount of oxygen in the weld, which is a function of the welding processes. [7] Figure 6 shows that inert gas welding process i.e., gas tungsten-arc welding (GTAW), plasma-arc welding (PAW), and gas metal-arc welding (GMAW) generally achieve welds with higher toughness than flux-based welding processes i.e., shielded metal-arc welding (SMAW), submerged-arc welding (SAW), and flux-cored arc welding (FCAW). The lower toughness obtained with flux-based welding process is not always indicative of sigma phase precipitation, but it could be attributed to the formation of micro-oxides at the grain boundaries. Therefore, the importance of supplementing impact testing with corrosion testing for welding procedure qualification as stated in ISO 17781.

The welds obtained with SMAW and SAW methods using proper welding procedures generally pass the impact testing requirements stated in ASTM A923 and ISO 17881. Welds obtained with FCAW may not pass these toughness requirements. FCAW is widely used for welding of thin-wall components in the flue gas desulfurization (FGD) and desalination industries, and the thinner welds can typically achieve acceptable toughness.

ASME Section VIII requirements for impact testing for DSS base and weld metals are given in UHA-51(d)(3)(a), which requires testing of DSSs with an effective thickness > 10 mm (3/8 in.) or for components with a MDMT < –29 °C (−20 °F). ASME B31.3 requires testing of welds when the MAT is < −29 °C (–20 °F) and of base metals when the MAT is below the minimum allowable temperature for the specific grade.

The maximum operating temperatures are limited by the susceptibility of the DSS to the 475 °C (885 °F) embrittlement mechanism (see 5.7) or other embrittlement mechanisms. Most codes applicable to refinery equipment and piping limit the maximum design temperature for various DSS grades to 260 °C to 340 °C (500 °F to 650 °F) to avoid these problems as listed on Table 4. Welds are more prone to sigma formation than base materials, and hence these temperature limits are especially important with welded components.

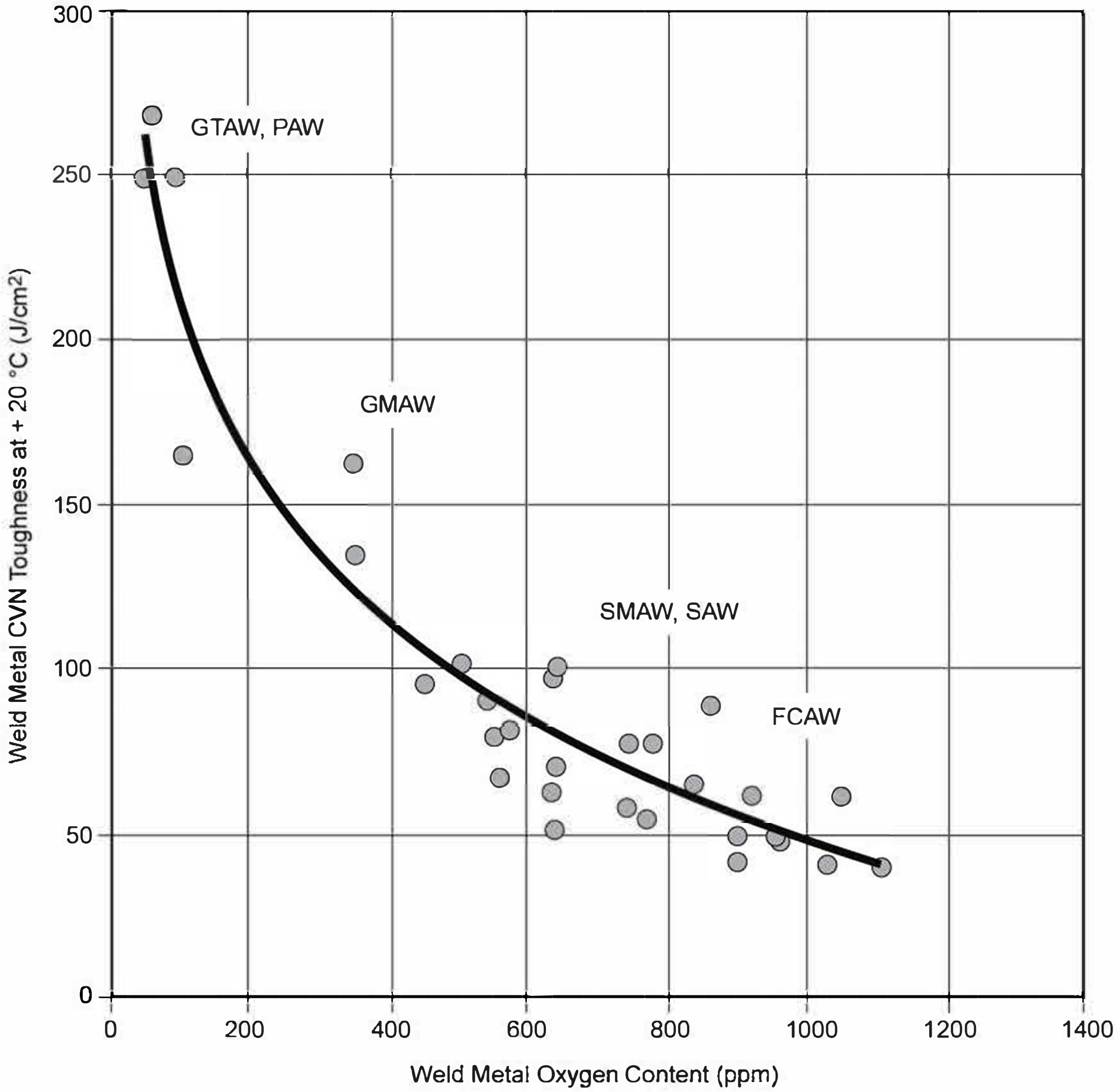


Figure 6—Effect of Weld Metal Oxygen Concentration on the Toughness of the Weld [7]

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	316 (600)
S32202	316 (600)	NL[a]
S32003	343 (650) Code Case 2503	343 (650)
S82011	343 (650) Code Case 2735	NL[a]
S82441	316 (600) Code Case 2780	316 (600)
S31803	316 (600)	316 (600)
S33205	316 (600)	316 (600)
S32550	260 (500)	NL[a]
S32750	316 (600)	316 (600)
S32760	316 (600)	316 (600)
S32906	316 (600)	316 (600)
S32707	260 (500) Code Case 2586	NL[a]
S83071	Pending code case	NL[a]

[a] NL = not listed.

4.5 Hardness Conversions

Hardness conversion between the Rockwell C, Vickers, and Brinell scales is different for DSSs compared with CS and other low-alloy ferritic steels.[2] This is an important consideration when hardness value limits from industry standards in Rockwell C are applied to weld procedure qualifications, which are typically tested using a Vickers method. The conversion chart given in ASTM E140 was developed for CS and low-alloy steels, but it is often used for DSS even though its use results in conservatively low Vickers values for DSSs. This effect is shown by the curves in Figure 7. For example, for a desired limit of HRC 28, CS should use 286 HV, while DSSs should use 334 HV. Also relevant for microhardness measurements is the possibility that the size and orientation of the two phases may be coarse relative to the indenter size in certain products such as cast DSSs.

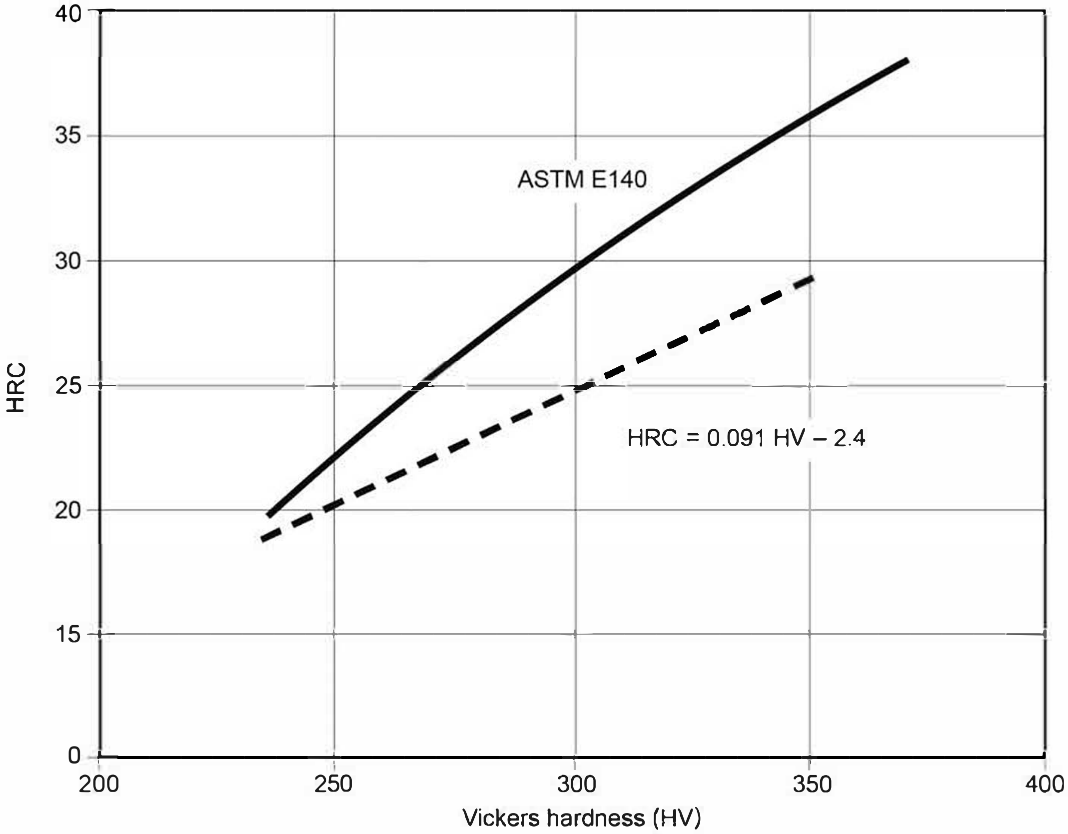


Figure 7—Compilation of Hardness Data for a Range of Duplex Parent Materials and Weldments Showing the Best-fit Line and ASTM E140 Conversion for Ferritic Steel [2]

There are ongoing studies sponsored by two alloy producers, as well as a round-robin study sponsored by ASTM that are looking at adjusting the hardness conversion formula in E140. An adjusted conversion formula may be available in the future.

Vickers hardness is the most practical and accurate hardness testing method for DSS welds, but sample preparation method and loads used for the testing can strongly affect the results. Low loads such as 500 g/HV0.5 are particularly necessary for accurate measurement of HAZ hardness.

5 Potential Environment-related Failure Mechanisms

5.1 Chloride Pitting and Crevice Corrosion

Because DSSs have higher Cr content than some 300 series austenitic stainless grades and because the duplex grades readily accept alloying with molybdenum and nitrogen, various DSSs grades have significantly better chloride pitting and crevice corrosion resistance than the standard austenitic SS, such as 304L and 316L (UNS S30403 and S31603). The most common tools for predicting the chloride pitting resistance of corrosion resistant alloys are the PREN and the critical pitting temperature (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 of these equations reported in the literature; however, the following are the most prevalent (with the second formula being used by many industry standards, including ANSI/NACE MR0103/ISO 17945).

$$\text{PREN} = \%\,\text{Cr} + 3.3 * \%\,\text{Mo} + 16 * \%\,\text{N} \tag{1}$$

$$\text{PREN} = \%\,\text{Cr} + 3.3*(\%\,\text{Mo} + 0.5*\%\,\text{W}) + 16*\%\,\text{N} \qquad (2)$$

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, due to differences in chemical composition between ferrite and austenite phases, each can have a different PREN. 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. In standard duplex SS grades, the austenite grains can have a lower PREN, and in the lean duplex SS grades, the ferrite grains can be lower PREN compared with the PREN based on overall chemistry. In some severe services such as some flue gas desulfurization units, this has led to selective attack of the phase with the lower PREN. Some examples of alloy partitioning for 25 Cr DSSs are shown in Tables 5a–5f, which is in 5.6.

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

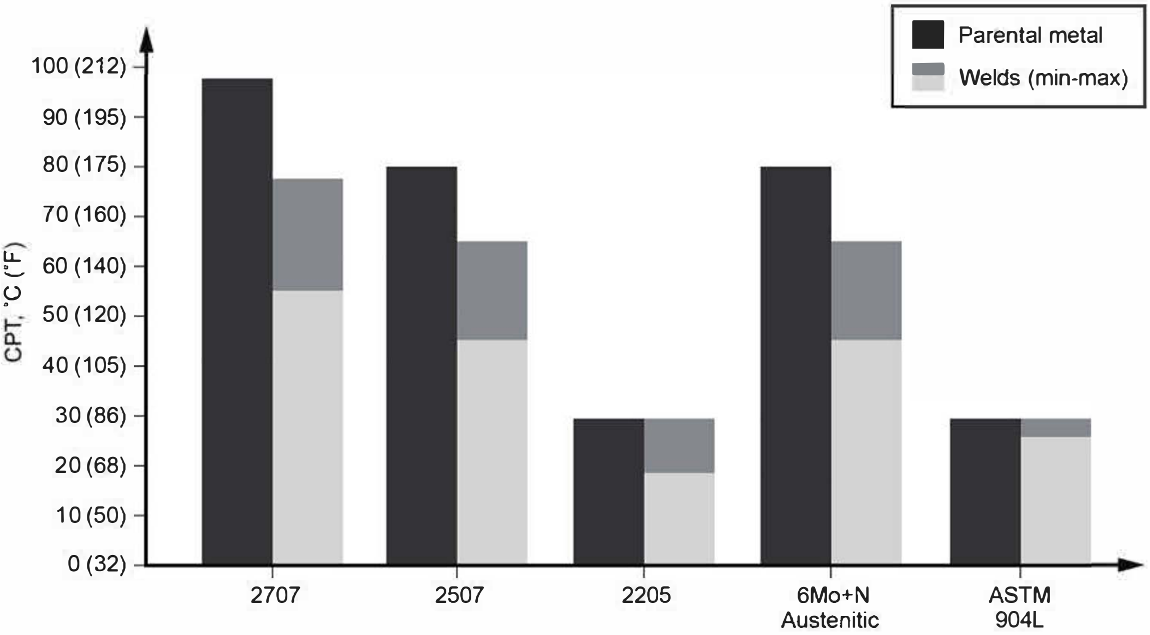


Figure 8—CPT for 22 % Cr, Super and Hyper DSS Alloys Compared with Austenitic SS Alloys in 6 % $FeCl_3$, ASTM G48 Test Method A[8]

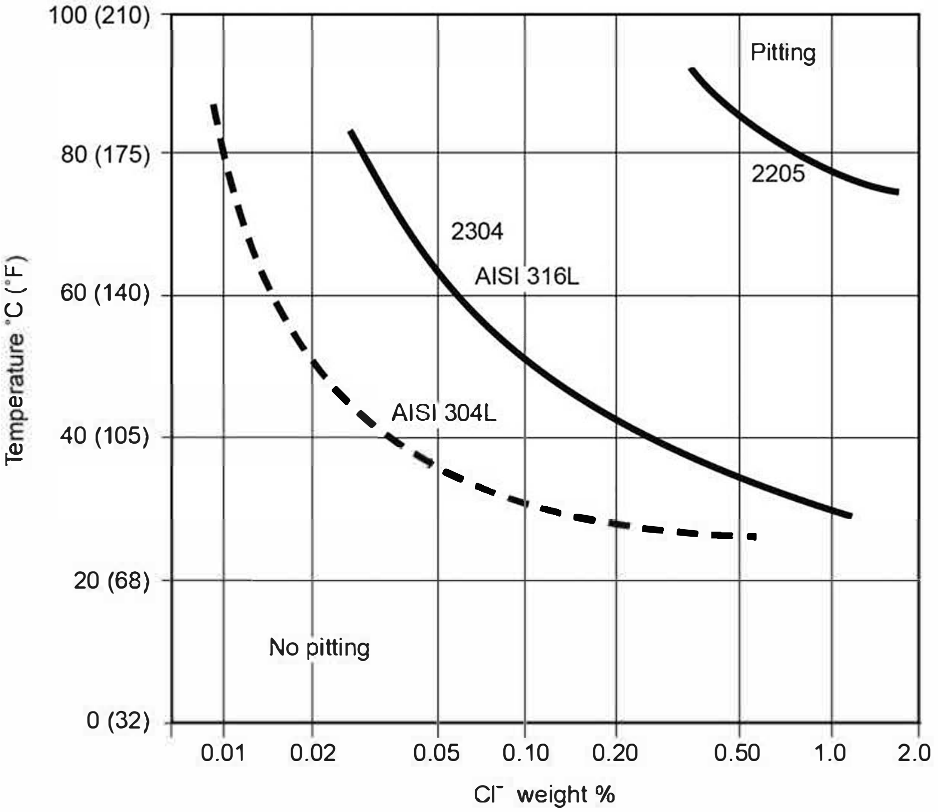
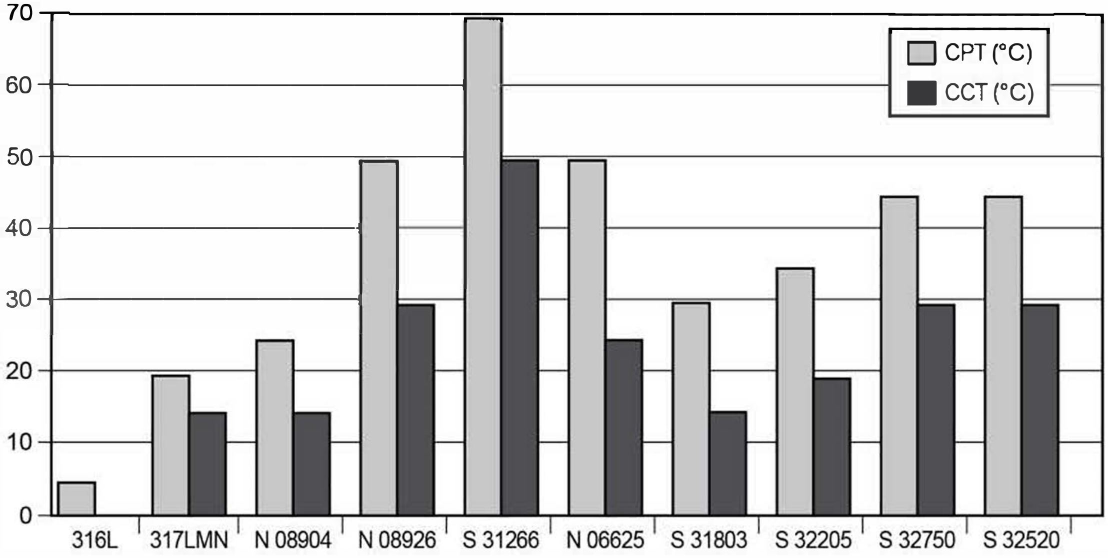


Figure 9—CPTs at Various Concentrations of Sodium Chloride (at +300 mV vs SCE, Neutral pH)[8]

One test program, targeted for the refining industry, measured the resistance of various alloys to 20 wt.% and 40 wt.% ammonium chloride solutions, and it showed excellent resistance of DSS with PREN of 40 or higher. [9] However, a second test program showed pitting of super DSS under an ammonium chloride salt deposit when the relative humidity was 50 % and 60 %; the testing was done at 80 °C (176 °F). This test program also studied the critical relative humidity (CRH) of ammonium chloride salt deposits at different temperatures, which also had an effect on the corrosion. [10]

Crevice corrosion resistance is similarly shown by a critical crevice temperature (CCT) that is commonly determined by the ASTM G48 Test Method F (formerly ASTM G48 Test Method D) test. This test gives lower temperature results, which indicate that it is a more severe test. Figure 10 shows CCT results on duplex and austenitic SS. The CCT is a function of the severity of the crevice, including the selection of the crevice forming material.



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

Figure 10—CPTs and CCTs for 22 % Cr and Super DSS Compared with Austenitic SS Alloys in ASTM G48 Tests [11]

5.2 Corrosion in Seawater and Microbiological Induced Corrosion (MIC)

Although the variables mentioned in 5.1 are important factors for corrosion resistance in seawater, experience has shown that DSS typically needs a PREN ≥40 to resist pitting and crevice corrosion in ambient temperature seawater. Seawater corrosion is a highly complex situation where aeration, filtration, biofouling, biofouling control, and salinity lead to corrosion behavior not necessarily directly proportional to temperature. This makes the acceptability of 22 % Cr DSSs difficult to predict. Thus, super DSSs (PREN > 40) are more commonly used in seawater heat exchangers and pumps. 27 % Cr hyper DSS are used in seawater applications at higher temperatures than super DSSs.

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

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

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

$$\mathrm{Ca^{2+}(aq) + 2HCO_3^-(aq) \leftrightarrow CaCO_3(s) + CO_2(g) + H_2O} \qquad (3)$$

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

In a modified version of ASTM G48A, test samples are exposed for periods of 24 hours in 6 % $FeCl_3$. This solution has a corrosion potential of +600 mV that is equivalent to continuously chlorinated seawater's potential. When pits are detected together with a substantial weight loss (> 5 mg), the test is interrupted. Otherwise, the temperature is increased 5 °C (9 °F) and the test is continued. The CPT of S32707 defined in this way was 97.5 °C (207.5 °F), compared with ~80 °C (176 °F) for S32750. **[12] [13]**

A typical limit for super DSS (with PREN ≥40) heat exchanger tubing in seawater is 60 °C (140 °F) at flow velocities of 5 ft./s (1.5 m/s) minimum. However, if there is a risk of deposits or if the seawater is chlorinated, the limit is suggested to be reduced to 50 °C (120 °F). An additional requirement is that incoming seawater should be filtered to reduce silt and sand deposits that promote corrosion. However, the calcium carbonate fouling described above cannot be prevented by filtration or maintaining flow rates and hence is typically the defining factor when it comes to using super duplex and other stainless steels in chlorinated seawater cooling applications. For seawater-cooled heat exchangers working with metal temperatures above this critical temperature of 60 °C (140 °F), there is thus a risk of under-deposit corrosion. Hyper DSSs show improved resistance and are being used in some cases up to 70 °C (160 °F), with or without continuous chlorination. [12]

When a biofilm grows on the surface of stainless steels, there is an increase of the open circuit potential (OCP). This ennoblement may cause local corrosion once the OCP reaches values exceeding the pitting or crevice potential of the steel grade [44]. Additionally, the formation of a biofilm may produce a crevice corrosion mechanism.

Industry experience suggests that alloys with a higher PREN are more resistant to MIC. Additionally, water treatment with biocides and systems design that minimizes low flow areas are necessary to prevent MIC [47]. It should be noted that treating with strongly oxidizing biocides that release chlorine byproducts can reduce MIC corrosion, but increases other forms of corrosion like pitting and crevice corrosion.

5.3 Chloride Stress Corrosion Cracking (CSCC)

Risk of CSCC restricts the use of standard austenitic SS grades such as 304L and 316L based on chloride concentrations, temperatures, and other factors. Depending on the chloride concentration in the bulk solution along with consideration of concentrating mechanisms (such as hot surfaces, under-deposit environments, or crevices), actual metal temperature, acidity/pH, tensile stress, time of exposure, and oxygen concentration, CSCC can cause rapid failures. In most cases, temperatures greater than 60 °C (140 °F) with chloride concentration as low as 50 ppm are a risk for cracking of those austenitic SS grades, with cracking tendency increasing with increasing metal temperature and chloride concentration. However, the risk of CSCC is dependent upon all of the listed factors, and in severe cases, CSCC can occur at slightly lower temperatures.

DSSs are a common "replacement" or alternative material in services where the threat of CSCC makes 300 series SSs a poor or marginal alloy choice. Practical experience and laboratory testing have shown the good resistance of DSSs to CSCC, but they are not immune. [8][14] Figure 11 and Figure 12 present results from tests that compared various grades of DSSs with other alloys in chloride solutions. Results from high-pressure autoclave tests in neutral, oxygenated chloride solutions are shown in Figure 11. [8] The tests indicate the comparative cracking thresholds vs chloride concentrations and temperatures for various alloys.

Figure 12 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. Test results show that DSSs have a much higher resistance to SCC under these conditions than austenitic SS.

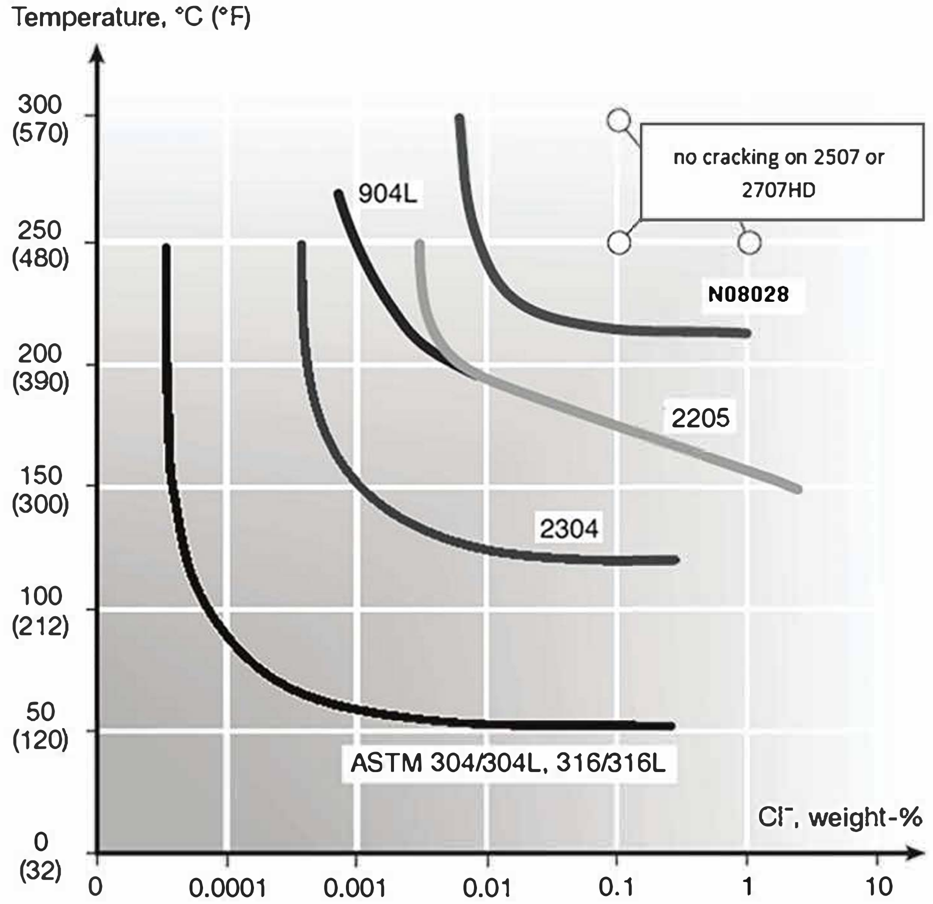


Figure 11—CSCC Resistance of DSS Alloys Compared with Austenitic SS Alloys in Oxygen-bearing Neutral Chloride Solutions [8]

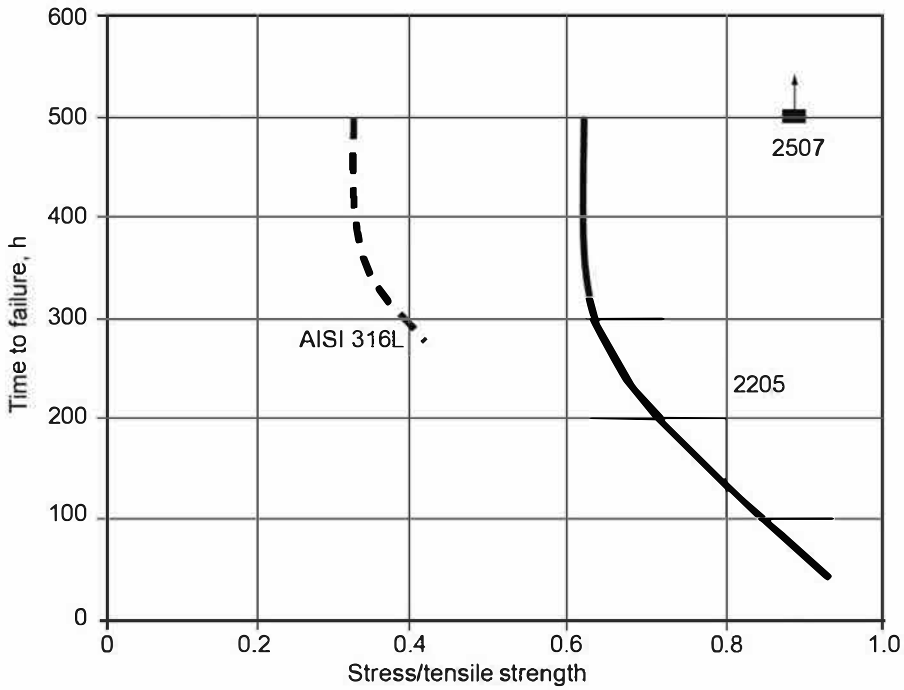


Figure 12—Results of SCC Tests of 22 % Cr and 25 % Cr DSS Alloys Compared with Austenitic SS Alloys in Constant Load Tests in 40 % $CaCl_2$, 1.5 pH at 100 °C with Aerated Test Solution [8]

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

1) Chloride concentration can build up under evaporative conditions, in the water film in contact with a heat-rejecting surface, under-deposits, or in a crevice. Cases of CSCC have occurred on standard and super DSSs that were exposed to chloride salt deposits resulting in extremely high localized chloride concentrations, and some of these cases were at surprisingly low temperatures. [15] [16] [17] [18] [19] Various types of chloride salts (e.g., Na, Mg, Ca, Fe, NH_4, Li, etc.) also showed variations in severity.

2) High pH environments (e.g., NH_4HS, amine, or caustic) are expected to have higher thresholds for CSCC than neutral or acidic solutions.

3) Wet–dry conditions as may occur when water cyclically contacts 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.

4) H_2S may interact with chlorides reducing the threshold at which CSCC may occur, especially in acidic (low-pH) conditions.

There have been reported failures of DSSs due to CSCC in the industry, but most are under severe conditions where SCC could be predicted. Some failures were attributed to external SCC on relatively hot equipment. Table 14 lists some examples of CSCC from refinery services reported in NACE Refin-Cor.

CUI can also lead to corrosion or CSCC of DSSs as discussed in 5.8.

5.4 Hydrogen Assisted Cracking (HAC)/Sulfide Stress Cracking (SSC)

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

The behavior of DSSs in aqueous solutions containing H_2S is dependent on the sulfide species (S^{2-}, HS^-, H_2S) present in the environment. In the water phase, there is a balance of H_2S, HS^-, and S^{2-}, as a function of the pH. The reactions for each pH level are described below:

$$\mathrm{Fe + H_2S = FeS + 2H^+ (acid\ pH)} \tag{4}$$

$$\mathrm{Fe + HS^- = FeS + H^+ + 2e\ (neutral\ pH)} \tag{5}$$

$$\mathrm{Fe + S^{2-} = FeS + 2e\ (basic\ pH)} \tag{6}$$

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

Numerous fabrication requirements can be specified to control ferrite content and minimize hardness, which reduces the susceptibility to SSC. There has been extensive testing performed on DSSs at acidic pH values to understand and avoid cracking. Although there is controversy on the laboratory test methods used and the ability to correlate their results to service conditions, these testing methods have allowed some limits to be established on the use of the different DSSs in wet sour services.

ANSI/NACE MR0103/ISO 17945 limits the maximum hardness for DSSs base materials in wet sour services to 28 and to 32 HRC for DSSs with PREN ≤40 and PREN >40, respectively. That standard also requires:

— base metal to be in the solution-annealed condition; and

— ferrite content between 35 vol % to 65 vol %.

Additionally, for materials in the as-welded condition, ANSI/NACE MR0103/ISO 17945 specifies that the average hardness at the weldment not exceed 310 HV and no individual reading exceed 320 HV.

ANSI/NACE MR0103/ISO 17945 was developed based on NACE MR0175/ISO 15156, and the two are often referenced when discussing material selection for sour environments in refineries. However, refining environments have significantly different conditions than oil and gas production environments; hence, the NACE MR0175/ISO 15156 limits are not specific for downstream applications. Oil and gas production environments typically contain carbon dioxide and bicarbonate ions and are lower than neutral pH, while many of the refining environments contain high amounts of ammonia and have a higher than neutral pH. Also, oil and gas production environments often contain significantly higher levels of chlorides.

For solution-annealed DSSs, NACE MR0175/ISO 15156 does not impose a hardness limit for the material to be suitable for use in H_2S-containing production environments regardless of chloride concentration and in situ pH, as long as the material has a ferrite content between 35 % to 65 % for wrought and cast materials and 30 % to 70 % for welds (excluding the HAZ). However, this standard limits the use of DSSs to temperatures up to 232 °C (450 °F) and H_2S partial pressure between 0.3 psi (2 kPa) and 3 psi (20 kPa) depending on respective DSSs PREN. In the case where the chloride concentration is expected to not exceed 50 mg/l, NACE MR0175/ISO 15156 does not impose any restrictions on temperature, H_2S partial pressure or in situ pH in production environments. These limits were developed specifically for the oil and gas production industry and were based on experience and laboratory testing focused on producing environments.

Table A.25 in NACE MR0175/ISO 15156-3:2015 applies to cold-worked DSS materials, but the title of the table indicates that it applies only to “downhole tubular, packers or other subsurface components”. For DSSs with various PRENs, limits are given on H_2S partial pressure, and in some cases, chloride concentrations, in addition to a hardness limit of 36 HRC maximum. Some users in the oil and gas production industry reportedly apply this table to additional cold-worked components besides those listed in the table title.

Some SSC failures in refinery applications have been attributed to improper fabrication, which led to ferrite contents and/or hardness levels in some zones of the weldment being outside the limits specified in ANSI/NACE MR0103/ISO 17945. The tight control of welding variables given in API Recommended Practice 582 for DSSs are there to ensure that the production welding satisfies the hardness and phase balance necessary to minimize the risks of SSC and other weld-related issues as described in 4.3.

Multiple weld cracking failures of DSS in hydroprocessing units have been attributed to HAC associated to welds and heat-affected zones in reactor effluent air coolers’ (REAC) headers and tube-to-tubesheet joints and associated piping. The equipment was exposed to severe refining environments containing high NH_4HS concentrations, high operating pressures with high H_2 partial pressures. Failure analysis completed on some of the incidents have attributed the cracking to poor fabrication practices that resulted in high ferrite contents in the weld or HAZ. The ferrite values on the available reports have shown ferrite contents between 63 % and nearly 100 % and/or high hardness up to 335 HV[42].

Some of the failures could not be traced back to poor fabrication practices [23]. The complex geometries associated with the heavy wall construction of the headers as well as the inability to perform ferrite measurements of the HAZ and hardness surveys of corner welds makes it impracticable to verify the effectiveness of good fabrication practices to achieve adequate phase balance.

The Materials Technology Institute in 2015 published the report “Fabrication of 2205 Duplex Stainless Steel REACs in Refinery Hydroprocessing Units”[50] summarizing the metallurgical findings of seven failures and providing additional base materials and fabrication requirements to help mitigate the risk of SSC and NH_4HS corrosion in these environments.

High ferrite content as well as high hardness values increase the susceptibility to SSC and hydrogen embrittlement. Additional research is needed on this topic to optimize not only the hardness limits but the ferrite content in refining sour services.

5.5 Ammonium Bisulfide Corrosion

There is laboratory data showing the resistance of DSSs to ammonium bisulfide corrosion, [24][25] and Tables 12 and 13 show extensive field experience with the use of DSSs in these environments.[26] Case histories come from hydroprocessing units, sour water stripper units, FCC units, and coker units. Duplex 2205 was one of the commonly used alloys for REACs under relatively severe conditions, and it has been shown to have just slightly lower corrosion resistance to ammonium bisulfide (NH_4HS) than alloy 825. Super DSS has shown to have a slightly superior resistance to NH_4HS than alloy 825 and alloy 625 and is just slightly inferior to alloy C-276 for this application. [24] Further information on the use and limitations of DSSs in REACs can be found in API Recommended Practice 932-B.

There are numerous case histories of duplex stainless steel's applications in hydroprocessing units with NH_4HS concentrations up to 10 %. However, it is important to consider that there are other critical variables affecting the acceptability of and threshold NH_4HS concentration for DSSs including velocity (shear stress), H_2S partial pressure, temperature, water injection distribution and contacting, water quality, chlorides, etc. A proprietary joint research program was sponsored by interested companies to collect data on NH_4HS corrosion. The program initiated in March 2000 and concluded the first phase of work in February 2003, and the second and third phases were completed shortly after. [27] The result of this work was a model that better defined the roles of several key variables affecting the corrosion behavior of different materials. Corrosion prediction software uses this model to predict NH_4HS corrosion rates for various materials. [25] Some new applications have used 9.1 m/s (30 ft/s) as the maximum velocity for standard DSSs; however, this limit may be conservative in many cases.

One case of DSS failing due to NH_4HS corrosion in a sour water stripper (SWS) is listed in Table 14; however, the NH_4HS concentration was not reported. The environment in SWS's is different than in REACs, as SWS environments are low pressure, do not have hydrocarbons, can have greater NH_3 than H_2S (in partial pressures), can have NH_4HS concentrations up to 25 %, etc. The corrosion prediction software mentioned above also gives guidance for SWS environments. [25]

In air coolers (especially REACs) where risks of wet ammonium chloride salt deposits exist, DSSs could also be susceptible to chloride pitting as discussed above in 5.1. These deposits are extremely corrosive to almost all alloys, and hence, preventing the formation of these deposits by process measures, such as water washing or maintaining a temperature above the salt deposition temperature, rather than attempting to prevent corrosion with metallurgical upgrades is a more effective mitigation practice. [27] The presence of cyanides at levels above ~20 ppm can greatly increase the risk of NH_4HS corrosion on almost all alloys, except the nickel-based alloy C family. DSS piping has shown cyanide-related NH_4HS corrosion in a sour water stripper overhead with 80–90 ppm cyanides. [28]

5.6 Naphthenic Acid Corrosion

Naphthenic acid corrosion occurs primarily in crude units due to organic carboxylic acids in the crude oil and distilled cuts. The temperature range where it occurs is ~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 acid species. Molybdenum content is an effective mitigating variable for naphthenic acid corrosion and alloys with 2.5 % minimum Mo typically provide acceptable corrosion resistance.

There is little published laboratory data and minimal documented empirical data for DSSs in naphthenic acid refining services. One case was reported in which hyper duplex, grade S32707 was successfully used in a crude preheater with conditions that promote naphthenic acid corrosion. Some industry materials experts believe DSS grades with ≥2.5 % Mo have good naphthenic acid corrosion resistance based on their alloy elements; however, partitioning on the molybdenum between the austenitic and ferritic phases needs to be considered.

Partitioning of the molybdenum between the two phases of DSSs could affect the overall naphthenic acid corrosion resistance. Early papers on DSS alloy development showed that the partitioning result in a ratio of 1.5 to 1.6 for Mo in the ferrite to austenite phases.[2][4] This means that the austenite phase may have as low as 38.5 % of the "bulk" Mo content. Tables 5a–5f show some examples of partitioning in various DSS alloys and welds.

Table 5a—Partitioning of Alloying Elements Between Phases in 25 % Cr Alloys[28]

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

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

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

Table 5b—Partitioning of Alloying Elements Between Phases in 22 % Cr Weld Metals (Approx. Wt. %) [29]

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 5c—Partitioning of Alloying Elements Between Phases in 22 % Cr Base Metal and SMAW Weldments with Varying Arc Energy (Wt. %)[29]

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.

Table 5d—Partitioning of Alloying Elements Between Phases in 22 % Cr Base Metal and GTAW Weldment (Wt. %) [29]

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

Table 5e—Partitioning of Alloying Elements Between Phases in 22 % Cr DSS Base Metal

Phase	Cr	Ni	Mo
Austenite Grain 1	20.90	6.64	2.48
Austenite Grain 2	20.09	6.99	2.22
Austenite Grain 3	20.04	7.01	2.19
Ferrite Grain 1	23.79	4.31	3.68
Ferrite Grain 2	23.61	4.36	3.73
Ferrite Grain 3	23.81	4.32	3.63

Table 5f—Partitioning of Alloying Elements Between Phases in 25 % Cr DSS Base Metal [30]

Phase	Cr	Ni	Mo	N
Austenite	23.5	8.2	3.5	0.48
Ferrite	26.5	5.8	4.5	0.06

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

5.7 475 °C (885 °F) Embrittlement

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

The susceptibility to degradation of the base materials due to short-term exposures is shown in Figure 13a and Figure 13b. [2][4] The 25 % Cr and 27 % Cr alloys are more susceptible to this embrittlement than are standard 22 % Cr and the lean duplex grades, and they can embrittle from a room temperature toughness level of >150 J to 27 J (111 ft-lb to 20 ft-lb) from 10 hours of exposure to 475 °C (885 °F). Similar levels of embrittlement would take >10,000 hours at 300 °C (570 °F) for standard DSS. This embrittlement will also occur more rapidly in weld metals than in base material.

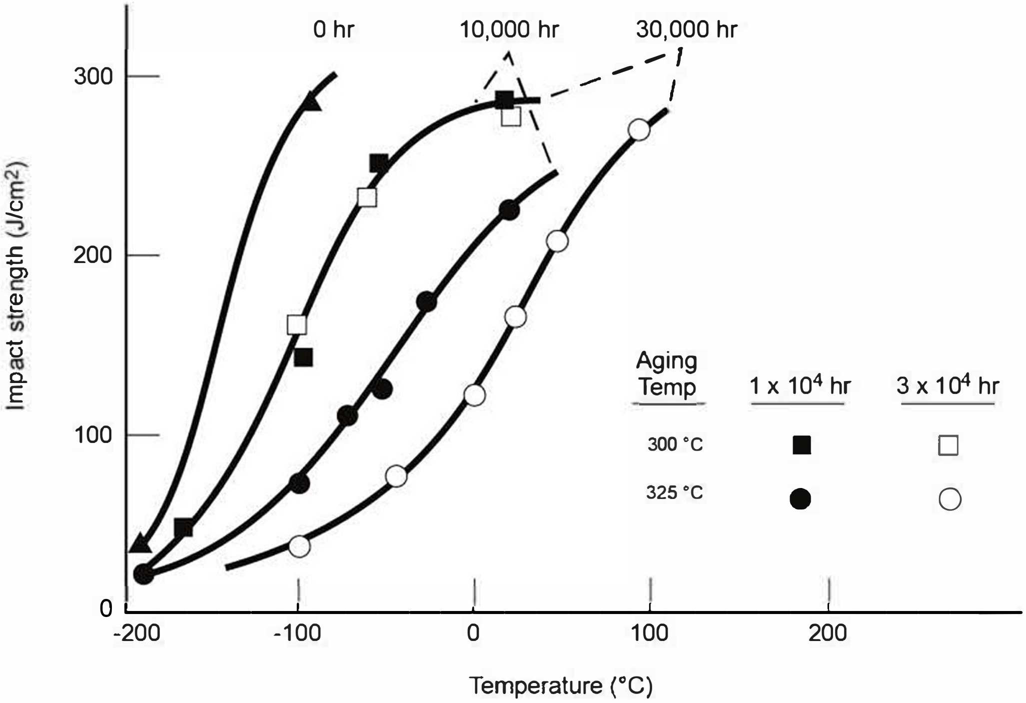


Figure 13a—Impact Energy Curves for Quench-annealed S32750 Alloy, Aged at 300 °C or 325 °C [°C = (°F – 32)/1.8][2]

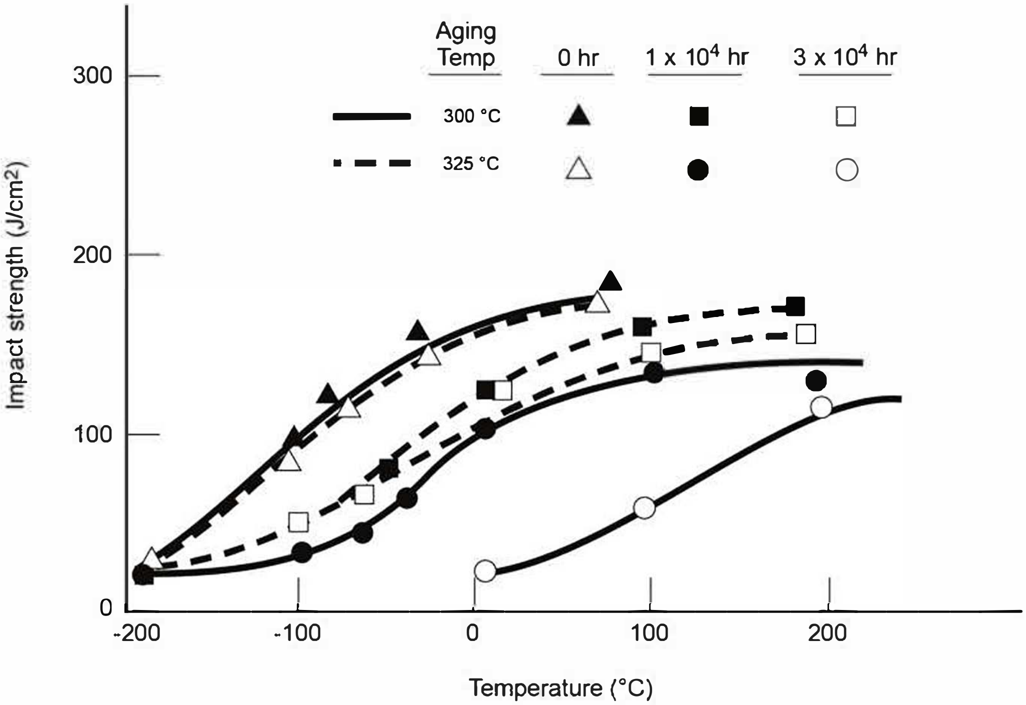


Figure 13b—Impact Energy Curves for 45 % Cold-worked S31803 Alloy, Aged at 300 °C or 325 °C [°C = (°F – 32)/1.8][2]

5.8 Corrosion Under Insulation (CUI)

Corrosion under insulation (CUI) is due to wet insulation forming aqueous chloride-containing solutions on the metal surfaces. These conditions can cause corrosion on carbon steel, austenitic SS, and DSS and can cause chloride stress corrosion cracking (SCC) on austenitic SS or DSS. NACE SP0198 addresses this concern and provides recommended coating systems.

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

For further information about this mechanism refer to API Recommended Practice 571, *Damage Mechanism Affecting Fixed Equipment in the Refining Industry*.

6 Material Specifications

6.1 Typical Specification Requirements for Wrought Materials

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

A minimum nitrogen content of 0.14 % in 22 % Cr DSS base metals is required in most refining services to ensure adequate ferrite content as well as corrosion and environmental cracking resistance at weldments. Therefore, if UNS S31803 that has an allowed nitrogen range of 0.08 % to 0.20 % is being used, its chemical composition needs to be restricted to 0.14 % to 0.2 % nitrogen. Most users have defaulted to only use UNS S32205, as it meets the required nitrogen content range as shown in Table 1. Alternatively, the use of dual certified grade UNS S31803/UNS S32205 is a common practice.

Water quenching after final anneal is another common requirement specified to ensure the desired corrosion resistance. This minimizes the time the DSS products are exposed to the 982 °C to 705 °C (1800 °F to 1300 °F) temperature range. However, thin sheet, strip, tubing and piping have been produced successfully by quenching with reducing gases. This process is known as “bright annealing” and results in products with smoother surfaces than those produced with water quenching and pickling. Bright annealing is performed in a vacuum or controlled atmosphere containing hydrogen. This practice is allowed by several of the wrought product specifications, including ASTM A480, ASTM A789, ASTM A790, etc. All of these permit either water quench or rapid cooling by other means. For other product forms of moderate thicknesses, water quenching is required as gas quenching will not yield the high cooling rates necessary to avoid the formation of intermetallic phases.

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 users’ specifications require a test to determine if such detrimental phases exist. If intermetallic precipitates are present, they will affect both low-temperature toughness and corrosion resistance in most aqueous services. The testing conditions for standard and super DSS are covered by ASTM A923, while ASTM A1084 offers guidance for some of the lean grades. Both standards include three acceptable testing methods as listed below. The specific testing method to be used needs to be agreed upon between the supplier and the end user.

1) Test Method A: Etch method for detecting the presence of potentially detrimental phases by microstructural evaluation;

2) Test Method B: Charpy V-notch impact test for determining the presence of detrimental phases by reduction in toughness;

3) Test Method C: Corrosion testing for determining the presence of detrimental phases by reduction in corrosion resistance.

Several refiners have opted to exclude test Method A as an acceptable testing method due to the potential bias on the interpretation of the microstructure, therefore defaulting to either test Method B or C. Alternatively, ASTM G48 practice A is also specified as a corrosion test to determine the presence of intermetallic phases. However, since this test method does not include an acceptance criteria for weight loss nor defines a testing temperature, the user needs to include those requirements in their specification.

ASTM A1084 only provides testing and acceptance criteria for base metal testing for grades UNS S32101, S32304, S32202, and S82011, and currently does not address welds. One paper studied the performance of lean duplex welds when using the ASTM A1084 testing Methods B and C and demonstrated that weldments that were produced following recommended welding procedure were able to pass the corrosion testing as specified for the base material. However, the weld metal showed lower toughness values than the acceptance criteria set for base metal.[33]

The acceptance criteria for various DSS base metals, welds, and heat-affected zones given in ASTM A923 were selected because they reliably correlated with the presence of intermetallic phases, and while it provides clear guidance and acceptance criteria for standard 22 % Cr DSS (e.g., 2205), it is not inclusive of all other DSS grades. In fact, ASTM A923 doesn't provide acceptance criteria for 25 % Cr, higher alloy welds, or HAZ, leaving it up to the end user to specify these values.

Because ASTM A923, A1084, and ASTM G48 testing conditions and acceptance criteria are not inclusive of all duplex grades and do not clearly differentiate between base metal and weldments, some companies have adopted different testing conditions and/or acceptance criteria for their wrought products and fabricated equipment. This approach has resulted in endless numbers of specifications limiting the ability to stock and procure readily available materials that satisfy individual requirements.

EPCs and fabricators reported multiple instances in which, due to lack of experience, end users have specified the same acceptance criteria for the welds and HAZ as those of the base metal, resulting in too-conservative testing, creating unnecessary recycle and rework during qualification and fabrication of end products.

ISO 17781 provides more inclusive testing and well-defined acceptance criteria for different DSSs. Similar to ASTM A923 and ASTM A1084, ISO 17781 provides guidance for microstructural, toughness, and corrosion testing and promotes the use of all three test methods to ensure the product is free of intermetallic phases. Furthermore, ISO 17781 provides acceptance criteria for ferrite content that is not included in either of the ASTM standards previously mentioned.

Even though the testing methodology presented in ISO 17781 cross-references ASTM A923, ASTM A1084, and ASTM G48, in some cases the acceptance criteria and testing condition in ISO 17781 may seem more or less stringent than those included in the ASTM standards. Although these values have been successfully used by several users and producers worldwide, it is the responsibility of each user to review, to understand, and more importantly, to confirm they are an acceptable alternative to the applicable ASTM or individual requirements.

If adopted, ISO 17781 could help align the materials requirements across all users, streamlining materials testing and potentially improving materials availability for the whole industry.

Due to the low wall thickness, neither ASTM A923 method B nor CVN impact toughness testing recommended on ISO 17781 apply to tubing. Therefore, the acceptance criteria to ensure mill tubing products comply with optimum corrosion resistance for refinery applications defaults to metallographic microstructural examination and ferric chloride corrosion testing per ASTM A923 Methods A or C or as defined by ISO 17781.

27 % Cr hyper DSS tubing is typically specified to pass an ASTM A923 Method C test, with a 24 hour exposure in a 6 % $FeCl_3$ solution at 80 °C (175 °F), and a criteria of weight loss of no more than 10 mdd.

Positive materials identification (PMI) testing is also specified by most purchasers to be done on all alloy pressure-containing base metal components and welds. It is a nondestructive test, and various details are given in API RP 578, *Material Verification Program for New and Existing Alloy Piping Systems*. This test helps ensure that the specified alloy grades are installed and avoids failures due to "mix-ups."

6.2 Welded vs Seamless Tubing and Piping

Many users allow either seamless or longitudinally welded tubing and piping. If GTAW, plasma arc welded (PAW), or laser welded tubing is allowed, some users require additional testing to verify the seamweld is free of defects, properly solution-annealed followed by rapid cooling, and free of detrimental phases. For the seamweld, corrosion testing in accordance with ASTM A923 Method C for DSSs and SDSSs, ASTM A 1084 Method C for LDSSs, or testing per ISO1778 is typically required. For welded tubing that will be rolled into tubesheets, seamweld bead working or tube redrawing is often recommended to avoid potential issues during tube-to-tubesheet rolling. Other users limit the weld root penetration to 0.004 in. or 6 % of the specified wall thickness, to mitigate the same issue. For nondestructive testing, an electric test (eddy current) and a hydrotest or air under water test are typically required.

Welded piping is either made with filler metal (ASTM A928) with options regarding annealing to be specified in the order, or without filler metal (ASTM A790) with the pipe to be fully annealed and quenched after welding. In some cases, the filler metal is an overalloyed 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.

6.3 Use of Integrally Finned Tubing

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

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

— Bare tube before finning Rc 30

— Fin valley Rc 44

— Middle of fin Rc 39

— Midsection of tube wall Rc 32

— ID of tube wall Rc 36

Since some of the cooling water bundles were in relatively severe services such as wet sour services, chlorides, ammonium bisulfide (with or without cyanides), various testing, as shown in Table 6, was conducted to analyze the susceptibility of the finned tubes to cracking.

Table 6—Summary of Corrosion Testing of Integrally Finned DSS (S31803/32205) Completed by One Refiner

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

These results show that finning did not affect the corrosion resistance of the tubes, as the finned tube corrosion rates matched that of the bare tube test specimens. The unacceptably high ASTM G48-A test results at 30 °C were expected, as explained in 5.1.

As demonstrated above, the hardness of the as-finned tubes does not meet the 28 HRC hardness requirement from ANSI/NACE MR0103/ISO 17945 for duplex with PREN <40. For this reason, another refiner developed and qualified an alternative manufacturing route that includes an additional off-line annealing step after finning 22 % Cr DSS tubes. The intent of the additional annealing process is to lower the hardness and to restore the mechanical properties and corrosion resistance of the finned tubes to satisfy the hardness requirements imposed by ANSI/NACE MR0103/ISO 17945.

Based on previous experiences, tubes in the as-finned condition were expected to pass the ASTM A923 weight loss requirement of 10 mdd. Hence, to verify the effectiveness of post-finning annealing step, it was deemed necessary to test the as-finned and the solution-annealed samples in a more aggressive solution consistent with ASTM G48 Practice E (6%$FeCl_3$ + 1%HCl). Table 7 presents the test results from the corrosion testing performed on bare tubes, as-finned and post-finned solution-annealed DSS 2205 tubes.

Table 7—Summary of Corrosion Testing Results of Low Finned Tubes in the As-finned Condition As Well As in the Annealed Condition after Finning

Sample	Condition	Time of Exposure	Test Temperature (°C)	Corrosion Rate (g/m²)	Visible Pitting at 20X	Pitting on Micrograph	Primary Location of Pitting
1	Control	24 Hours	25	0.7	No	No	—
2				1.2	No	No	—
3				0.4	No	No	—
1	As-Finned	24 Hours	25	5.7	No	Yes	Fin peaks
2				6.1	No	Yes	Fin peaks
3				5	No	Yes	Fin peaks
1	Finned + Solution-annealed	24 Hours	25	0.3	No	No	—
2				0.3	No	No	—
3				0.2	No	No	—

The test results presented in Table 7 demonstrate that the additional post-finning solution annealing step reestablishes the alloy's properties, avoiding the presence of intermetallic phases on the microstructure and improving the corrosion resistance behavior between the as-finned tube and the finned and annealed tube. Both performed consistently with results achieved for the control/bare tube.

6.4 Use of Twisted Tubes

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

In another case where 2205 twisted tubes were used in crude unit overhead service, the tubes failed by under-deposit chloride pitting in 18 months (which may have been unrelated to the "twisting") and were replaced by twisted tubes of hyper DSS grade S32707.[34] Before these tubes were installed, ASTM G48 Method A tests were done at 80 °C, along with hardness and ASTM A923 Method A tests. The results are presented in Table 8 and Table 9.

Table 8—Average Hardness Values of Hyper DSS S32707 Twisted Tubes

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

Table 9—Summary of Ferrite Content and Corrosion Testing Results per ASTM G48-A on Hyper DSS S32707 Twisted Tubes

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

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

6.6 Duplex SS Castings and HIP Components

Annex D provides an example of typical requirements for DSS castings for items such as valve bodies and pump cases in critical services. Annex D does not cover centrifugally cast line pipe. Annex E provides another example of typical requirements for DSS HIP components.

6.7 Duplex SS Used as a Cladding Material

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

The full range of DSS cladding thickness applied by the explosion-cladding process has been ~3 mm to 19 mm to date, and there are also cases of titanium cladding being explosively applied to DSS base metal with thicknesses of 25 mm to 152 mm. Some users have been able to capture significant savings by using DSS materials as backer of titanium explosion-bonded tubesheets instead of solid titanium tubesheets. When titanium

(Ti) is explosion clad on DSS, often a nickel intermediate binder is used, because it is difficult to get a good bond between the Ti and DSS without the use of a nickel binder.

7 Special Considerations during Fabrication of DSSs

7.1 Welding Procedure Qualification (WPS/PQR)

The following are examples of typical testing and specification considerations used during welding procedure specification (WPS)/procedure qualification record (PQR) (in addition to applicable Code requirements qualification:

1) added essential variables for each process (refer to API Recommended Practice 582 for a complete list of those);

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

   a) ASTM A923 or ASTM A1084 (as applicable): Test Method B and/or Test Method C for standard and lean DSSs; and both tests for 25 % Cr and higher alloys with criteria to be agreed to by purchaser; or ISO 17781;

   b) microstructure: measurement of intermetallics and percent ferrite from point count (see 7.7);

   c) hardness survey for sour services as defined per ANSI/NACE MR0103/ISO 17945;

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

7.2 Welding

The following are examples of typical considerations used in the development of specifications for welding in addition to applicable Code requirements:

1) cutting and joint preparation restrictions;

2) welding process restrictions;

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

4) the maximum and minimum heat input;

5) a maximum interpass temperature;

6) GTAW root passes for single-sided welds with filler addition and cold-pass technique;

7) the backing and shielding gas compositions;

8) heat tint removal on process side when accessible;

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

7.3 Tube-to-tubesheet Joints

Although there is not an industry consensus on best practices or standardized procedures for the specification of tube-to-tubesheet joints, users and fabricators report achieving successful results by both welding and tube expansion techniques. The following are some of the reported practices:

— For welding, limit usage of tube expansion except for a light rolling (<2 %) for tube positioning into the tubesheet, and require use of strength welds with filler metal. This practice is intended to avoid potential high hardness due to cold work of the tubes.

  — Select filler materials for tube-to-tubesheet joints based on process compatibility and fabricator experience. Some common filler materials used include ER309LMo, ER2209, ER2594, and NiCrMo-14 among others.

  — Use shield gas with up to 2 % nitrogen to further promote the formation of austenite in the welds.

— For tube expansion, allow the use of rolled joints with tube wall reduction between 6 %–8 % or rolled and welded joints with prequalification mockup tests, including hardness testing; However, a leading air cooler fabricator in Europe reported successful experiences with wall reduction up to 10 %.

— Require completion and testing of mock-up, regardless of the type of joint selected. Common testing may include evaluation for intermetallic phases, hardness surveys, ferrite content, and pull test

A study completed by one heat exchanger fabricator showed that rolls completed with parallel pin expander achieve the target wall reduction of 6 % to 8 % while maintaining the average hardness of 2205 duplex tubes below 300 HV10 with a maximum hardness of 316 HV10. However, when using the 3-pill tapered expander (self-feeding), the average hardness was 312 HV10 with a maximum hardness of 342 HV10.

7.4 NDE Methods

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

7.5 Typical Welding Processes and Filler Metals

The acceptable welding processes include GTAW, SAW, GMAW, SMAW, and FCAW (see 4.4). Commonly used filler metals are shown in Table 10. Even though the weld filler metals used for welding of standard duplex SS grade 2205 has higher nominal nickel content (9 %) than the base metal (5 % nominal), they are often referred to as "matching."

Table 10—Welding Consumables

Process	22 % Cr	25 % Cr[a]	27 % Cr
SMAW	SFA 5.4 E2209	SFA 5.4 E2553, E2594 or E2595	Not applicable
GTAW/GMAW	SFA 5.9 ER2209	SFA 5.9 ER2553, or ER2594	As recommended by alloy supplier
SAW	SFA 5.9 ER2209 with a flux designed for DSSs	SFA 5.9 ER2594 with a flux designed for DSSs	As recommended by alloy supplier
FCAW	SFA 5.22 E2209TX-X or EC2209	SFA 5.22 E2553TX-X, E2594TX-X, EC2553 or EC2594	Not applicable

[a] This table does not cover some of the specialized 25 % Cr alloys, and the material manufacturer (i.e., the alloy supplier) recommendations on welding consumables should be followed.

7.6 Dissimilar Metal Welding

For dissimilar metal welding, it is possible to weld DSSs to carbon steel, alloy steels, austenitic SS, and other grades of DSSs (although PWHT requirements need to be considered). The more important factors in selecting a filler metal are to obtain a weld with strength and corrosion resistance superior to at least one of the dissimilar base 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 DSSs 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 DSSs in Table 10. Manufacturer recommendations are typically followed when welding DSSs to other alloys, along with the recommendations in API Recommended Practice 582.

When welding DSSs to carbon or alloy steels, consideration is usually given to the potential detrimental effects on the DSS of the preheating or PWHTs required by the carbon or alloy steel. Preheating may slow the cooling of the DSS HAZ enough that intermetallic phases form. Most PWHTs for steel will lead to formation of intermetallic phases in DSSs. It may not always be possible to weld DSS to carbon or alloy steel and have both sides of the weld in an optimal metallurgical condition. One solution is to butter the CS or low alloy with austenitic filler metal (e.g., E309L) and PWHT and then weld to the DSS using a DSS filler metal. A similar approach has been used when overlay with DSSs is desired but the base metal would need to be PWHT, due to Code requirements. In those cases, a first pass of 309LMo is applied, then the assembly is PWHT per Code, and a final pass or passes of DSS or SDSS filler material is applied.

In some cases, Ni-based filler metals are proposed for either dissimilar metal welds or duplex welds. However, Ni-based fillers may give rise to a fully ferritic zone adjacent to the fusion line in DSS that would not meet the desired ferrite requirement. This zone also tends to give reduced toughness of the weldment. There can also be intermetallic phases formed in the weld, resulting in reduced corrosion resistance. Nickel-based filler metals containing niobium (Nb) i.e., ENiCrMo-3 have reportedly resulted in low weld toughness and solidification cracking due to the precipitation of niobium nitrides. Other high-Cr, high-Mo nickel-based filler metals (with <0.5 Nb) such as ENiCrMo-4, ENiCrMo-10, ENiCrMo-13, and ENiCrMo-14 have been used successfully.

7.7 Ferrite Measurements vs Austenite Spacing

Achieving the proper phase balance in welds and HAZs is a critical step during welding. Welding procedure qualifications are performed to ensure welding parameters used during fabrication will result in an optimal phase balance. This phase balance is confirmed by performing ferrite measurements on the welding coupons. The methods used to measure the phase balance during welding procedure qualification include either microstructural analysis per the ASTM E562 manual point count method, computerized image analysis per ASTM E1245, or magnetic measurements with specialized devices.

When obtaining ferrite measurements by the ASTM E562 manual point count testing method, an experienced laboratory should be used. Obtaining a proper etching is important for this method, and one expert reported that doing an electrolytic etch in 10 % oxalic acid prior to the NaOH or KOH etch results in the phases standing out better (oxalic acid clearly shows the phase boundaries and the presence of any nitrides, which will not show with caustic etching alone).

7.8 Cold Working and Cold Bending

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

Heat exchanger U-bends are difficult to heat treat without some zone of the tubes being exposed to unacceptable temperatures, which results in impaired corrosion resistance due to the formation of detrimental phases during the heat treatment operation. Some refiners have successfully limited the heat treatment requirements to just

U-bends with a bend radius <5 times the outside diameter and reserved the right of reviewing and approving the heat treating procedure.

In the cases where the heat treatment of U-bends is specified, resistance or capacitance heating has been used successfully with procedures carefully designed to minimize the time of tube exposure in the 700 °C to 950 °C (1300 °F to 1750 °F) temperature range. Other heat treatment methods such as furnace heat treatments should not be specified, as this method typically only requires the bends to be inserted into the furnace, causing the tangent lengths to be exposed to an unacceptable and detrimental temperature for the material.

To prevent oxidation of the tube internal diameter (ID) during the annealing process, the tube ID is purged with a reducing gas (e.g., a combination of hydrogen and nitrogen, argon, etc.) to displace all the oxygen from the ID of the tube. The reducing gas blanket is kept during the heat treatment process (e.g., during heating, holding, and cooling) until the temperature during cooling down reaches 315 °C (600 °F).

Some users require corrosion testing of coupons taken from one U-bend tube (as described in 6.1) at two additional locations. One coupon is taken from the U-bend section and the other taken from the straight tube leg adjacent to the electric resistance (ER) clamp location.

Testing has shown that the properties of the U-bends without heat treatment are acceptable for refinery services where chloride stress corrosion cracking is a concern, as long as the bend radius is at least 1.5 times the tube diameter for 25 % Cr super DSSs grades and at least 3.3 times the tube diameter for S32205. Hence, various users have adopted the practice of not requiring the heat treatment of U-bends, as long as there is a 3.3D minimum radius for 2205 DSS; however, this may require the redesign of the inner row section of the exchanger in a way that allows for the installation of fewer tubes with the U-bend positioned diagonally to accommodate this larger minimum radius. [38]

Work done independently by two tube suppliers investigated whether or not stress relieving of tight U-bends in 25 %Cr super DSS was required for wet H_2S services. The testing included one tube size and two different thicknesses, ¾ in. OD x 0.065 in. wall thickness (19.05 mm x 1.65 mm) and ¾ in. OD x 0.095 in. wall thickness (19.05 mm x 2.41 mm).

The bent schedule selected for the study included bend radii of 1.5D (1.125 in.), 2D (1.5 in.), 3D (2.25 in.), 4D (3.0 in.), and 5D (3.75 in.). The tube samples were cold bent without stress relieving and then were subjected to a thorough hardness survey including multiple measurements in the compression, neutral, and tension axes of the bends (see Figure 14 and Figure 15). Additionally, corrosion testing per ASTM G48 Method A at 50 °C (122 °F) for a period of 24 hours was performed. The results are summarized in Table 11.

Even though API Standard 660 limits the bend radius to a minimum of 2D, the 1.5D bend radius was chosen to test the material under more severe conditions within the practical limits of bending capabilities.

Figure 14—Average Hardness (HV) on Super Duplex (UNS-S32750) Tubes after Bending to Different Bending Radius from 1.5OD to 5OD (Tubes Were 0.75 in. [19.05 mm] OD x 0.065 in. AW [1.65 mm])

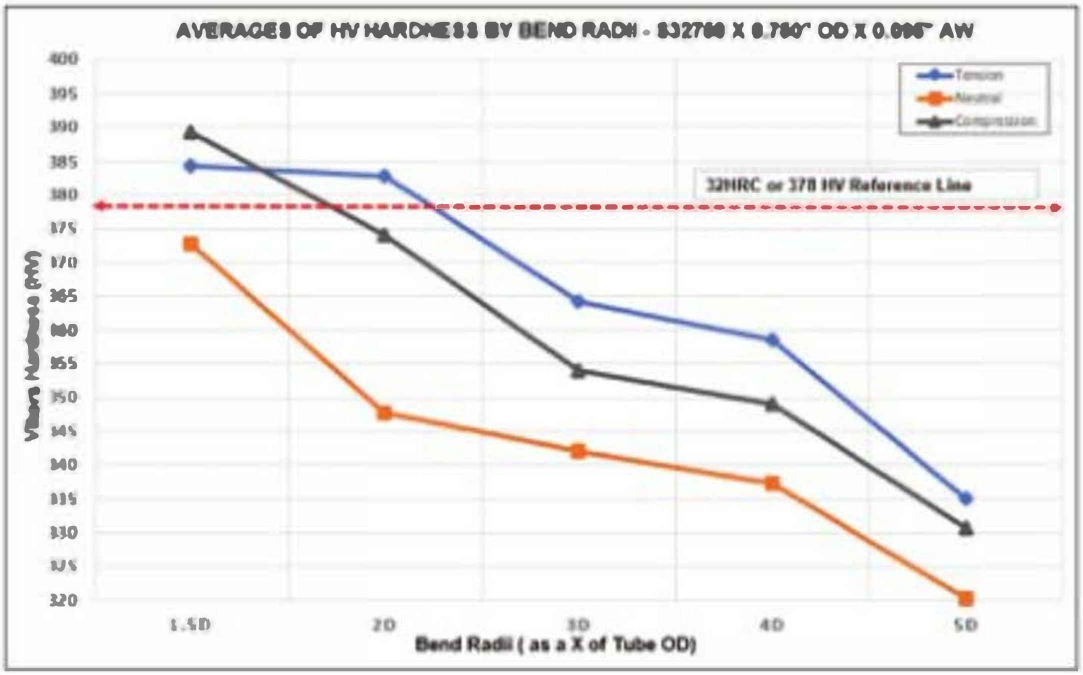


Figure 15—Average Hardness (HV) on Super Duplex (UNS-S32750) Tubes after Bending to Different Bending Radius from 1.5OD to 5OD (Tubes Were 0.75 in. [19.05 mm] OD x 0.095 in. AW [2.14 mm])

Table 11—Summary of Corrosion Test Results of Super Duplex Tubes in the As-bent Condition

Tube Dimension	Bend Radii 1.5 D		Bend Radii 2D		Bend Radii 3D		Bend Radii 4D		Bend Radii 5D	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
0.750 in. OD X 0.065 in. W	0.2	0.4	0.5	0.5	<1.0	<1.0	0.9	0.2	0.9	0.2
0.750 in. OD X 0.095 in. W	0.4	0.4	0.1	0.3	<1.0	<1.0	<1.0	0.8	1.1	0.6

NOTE 1 Samples with < 1.0 mdd reporting were estimated based on weight gain of < 1.0 mdd.

NOTE 2 For sample failure determination, acceptable criteria was no visible pitting and weight loss of less than 10 mdd (or 1 g/m^2).

As seen in Table 11, all of the as-bent samples passed the acceptance criteria of no visible pitting and weight loss less than 10 mdd despite the increased cold work expected from tight bend radii of 1.5D and 2D. The tight bend radius of 1.5D resulted in an average compression and tension axes hardness level significantly higher than the recommended threshold of 32 HRC or 378 HV for super duplex grades. These results indicate that the cold deformation achieved does not alter the corrosion performance of the material.

These results are in line with a previous study performed by one of the tube suppliers in which it had been demonstrated that cold deformation resulting from tight bends of super DSS up to 1.5D has no impact on the CPT and CISCC resistance of the material. However, the aim of this additional study was to evaluate the performance of such tight bends in refinery sour water services, and therefore the samples were further tested for SSC per NACE TM0177 Method C.

A total of 24 non-stress relieved U-bend samples were exposed to a modified (NaCl acidified) TM0177 Test Solution A. Twelve samples were tested at 25 °C (77 °F) and twelve samples were tested at 90 °C (195 °F) with a gas composition of 20,000 ppm H_2S in nitrogen. The final pH value for the solution tested at 25 °C (77 °F) was 3.6 and the pH value for the solution tested at 90 °C (195 °F) was 3.0 . Each temperature batch contained at least one sample for each bend radius without applying additional stresses.

All of the as-bent seamless S32750 super duplex tube samples passed SSC testing in a 20,000 ppm H_2S environment at both the 25 °C (77 °F) and 90 °C (195 °F) temperatures. The different stress levels created by various U-bend radii, including 1.5D and 2D, with hardness value above the recommended threshold, did not affect the result. [48]

Based on this study, 25 % Cr duplex stainless steel tubing bent to tight bend radii down to 1.5D and without heat treatment are suitable for refinery sour services.

In a follow up study, a similar hardness and SSC study was performed on standard and additional super DSS tubes. U-bend samples were produced using seamless stainless steel tubes UNS S32205 in 0.750 OD x 0.083 in. AW (19.05 OD × 2.10 mm AW) and UNS S32750 in 0.750 OD x 0.065 in. AW (19.05 OD × 1.65 mm AW). Test tubes were bent using bend dies with radii of 1.125 in. (28.57 mm), 1.500 in. (38.1 mm), and 2.250 in. (57.15 mm). Each representing bend radii of 1.5D, 2D, and 3D times the tube diameter of 0.750 in. (0.019 m). Post-bend heat treatment of stress relief of the bend was not performed. The work hardening effect on the standard DSS tubes can be seen in Figure 16, which demonstrates the increase of hardness values from the cold bending operation.

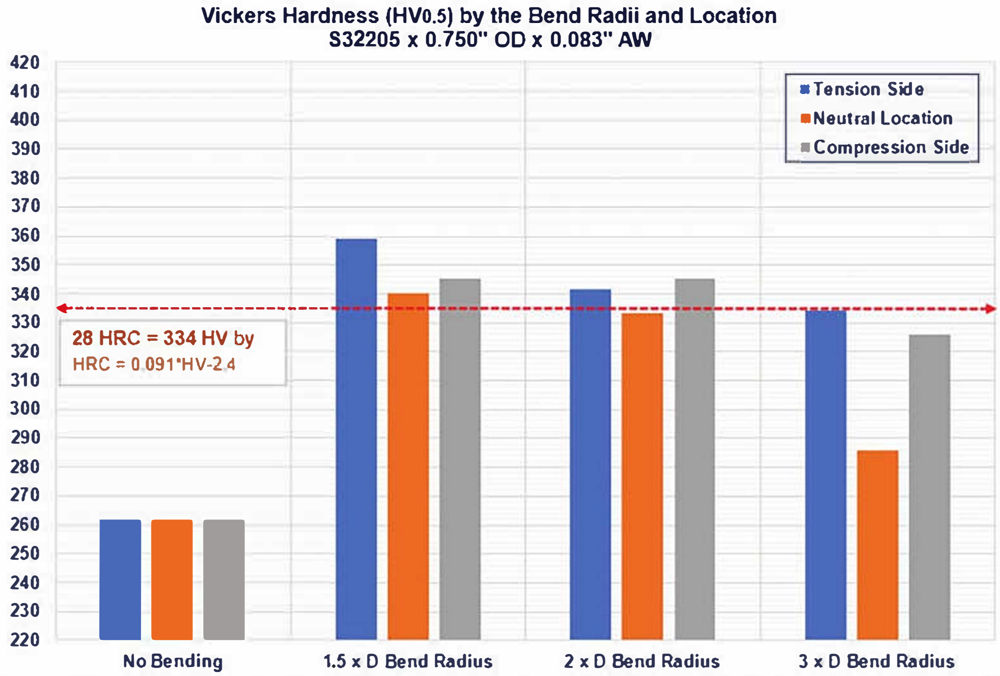


Figure 16—Work-hardening Effect on Standard 22 % Cr DSS Tubes by Bend Radius

In this study, corrosion testing was performed according to ASTM G48 Method E (acidified ferric chloride solution) on as-bent and as-finned S32205 and S32750 tubes. No pitting corrosion was observed in any of the samples tested. Table 12 and Table 13 show the results from this test.

Table 12—Pitting Corrosion Tests Results for S32205 and S32750 U-bend Specimens

Grade	ASTM G48 Test Parameters for 6 % FeCl3 + 1 % HCl	Bend 1 1.5 x OD (1.125 in.)	Bend 2 2.0 x OD (1.500 in.)	Bend 3 3.0 x OD (2.250 in.)
S32205	25 °C (77 °F), for 24 h	No Pitting	No Pitting	No Pitting
S32750	40 °C (104 °F), for 24 h	No Pitting	No Pitting	No Pitting

Table 13—Pitting Corrosion Testing for S32205 and S32750 As-finned Tubes

Grade	Test Parameters for 6 % Fe3Cl + 1 % HCl	As-finned Sample 1	As-finned Sample 2
S32205	25 °C (77 °F), for 24 h	No Pitting	No Pitting
S32750	50 °C (104 °F), for 24 h	No Pitting	No Pitting

Additionally, the tube samples were tested according to NACE TM0177 Solution A (acidified NaCl). The standard test gas was modified from 100 % H2S to 60,000 ppm H_2S in nitrogen. After 30 days exposure, the final pH of the solution was 3.05. No visually discernible cracks were observed in any of the samples. This study demonstrates that as-bent S32205 and 32750 with hardness values up to 34 HRC DSS are not subject to SSC under the conditions selected in this study[49].

7.9 Hot Bending

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

7.10 Post-fabrication Cleaning

The main objectives of post-fabrication cleaning are to:

— remove significant welding heat tints;

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

— remove surface contamination from smeared or embedded iron;

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

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

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

— blasting;

— grinding;

— pickling and passivation;

— electropolishing.

The best corrosion resistance is obtained by mechanical cleaning followed by chemical pickling and passivation. [40]

7.11 Hydrostatic Testing

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

7.12 Coating Requirements and Risk of CUI

Duplex SS components that are insulated and in an area where the climate or atmospheric conditions and the operating temperature range create a risk of external corrosion or chloride SCC due to CUI (see 5.1) are typically externally protected in a similar manner as austenitic SS. NACE SP0198, *Control of Corrosion Under Thermal Insulation and Fireproofing Materials—A Systems Approach* addresses this concern and gives recommended protection systems. Noninsulated DSSs are typically not coated, as they have excellent atmospheric corrosion resistance.

8 Examples of DSS Applications within Refineries

Numerous data sources were reviewed to compile a list of past uses of DSSs within refineries. One source that provided many case histories was NACE International's Refin-Cor database. Refin-Cor is a compilation of ~50 years of meeting minutes from the Refining Industry Corrosion Group. Table 14 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 15 shows other case histories from various published and unpublished sources, such as DSS material suppliers' case history reports and published literature primarily from users.

A list of the applications and the corresponding corrosion or other failure mechanisms that led to the selection of DSS is shown in Table 16. 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 14. Also, failures could occur in almost all services if DSS has poor material quality or is improperly fabricated.

Table 14—Case Histories of DSS Uses Reported in NACE International Refin-Cor

Item No.	Unit	Service	Grade	Problems	Comments
02F5.19–36	Amine	MEA Reclaimer	2205	None	Replaced 300 series SS which suffered Cl SCC
08C4.24–11	Amine	MEA Reclaimer	2205	Pitting in ends of U-bends (150 mm lengths) due to improper heat treatment. Remainder of tube "working very well"	No longer using heat treatment of 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 that 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	Freshwater 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 were found to be cost comparable to brass and readily available
08C4.16–10	Cooling Water	Critical bundles in freshwater CW service	2205	None	Replacing CS bundles that were not lasting for two runs

Table 14—Case Histories of DSS Uses Reported in NACE International Refin-Cor (Continued)

Item No.	Unit	Service	Grade	Problems	Comments
08C4.16–17	Cooling Water	Numerous bundles in freshwater CW service	2205	None	Recently did internal survey; no signs of MIC; good service; replace CS tubes (reusing CS tubesheets) regularly; cost is about twice compared with using CS tubes.
80C5.2–04	Crude	Overhead condenser and desalter effluent exchanger	3RE60	One manufacturing problem	—
80C5.2–05	Crude	Desalter effluent exchanger and top P/A exchanger	3RE60	OK in desalter effluent; failed faster than CS in top P/A due to hot chloride pitting	—
80C5.2–06	Crude	Overhead	3RE60	None	Test tube; showed 2 mpy to 3 mpy
87F7.1–13	Crude	Overhead condenser	3RE60	Failed by SSC in a few months	Test tubes
89C7.2–09	Crude	Tower top lining	2205	None	Previous sulfur corrosion of Monel™[1] 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	DSSs	None	Replaced Monel™[2], which corroded due to evaporating sour water and deposited salts

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[1] Monel is used strictly as an example of any nickel-copper alloy 400 matching UNS N04400 specifications. It does not constitute any endorsement of any specific product or company by API.

[2] Monel is used strictly as an example of any nickel-copper alloy 400 matching UNS N04400 specifications. It does not constitute any endorsement of any specific product or company by API.

Table 14—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 alloy 28
10C4.19–01	Flare gas recovery unit	Coker flare gas recovery liquid ring compressor impeller	Cast duplex SS	None	Previous cast 316 SS impeller failed by chloride SCC. They have numerous flare gas recovery liquid ring compressors made of DSS.
98F5.8–01	HDS	REAC	3RE60	CSCC under-deposits	At 300 °F to 400 °F where deposits collected
98F5.8–02	HDS	Exchanger	2205	SCC that initiated 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

Table 14—Case Histories of DSS Uses Reported in NACE International Refin-Cor (Continued)

Item No.	Unit	Service	Grade	Problems	Comments
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)
00F5.8–12	HDS	REAC outlet piping	2205	None	Replaced corroded CS. NH_4HS is 8 % to 10 %, with 18 fps to 20 fps and water wash
04F5.7–31	HDS	REAC	2205	None. 2205 tubes in CS header boxes. Also in cat feed HDS and hydrocracker	Tubes were seal welded to header box. In one case, the CS header suffered nozzle corrosion due to NH_4HS
86F7.3–02	HDS—Cat Feed	Feed/effluent (?)	3RE60	Good	CSCC of austenitic SS. Test tubes
73F8.4–01	Hydrogen Plant	MEA reboiler	3RE60	None	Previous SCC of 304 SS with 1000 ppm Cl
97C5.7–03	Hydrogen Plant	Pot. carbonate CO_2 removal reboiler	2507	None	OK after five 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

Table 14—Case Histories of DSS Uses Reported in NACE International Refin-Cor (Continued)

Item No.	Unit	Service	Grade	Problems	Comments
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
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 15—Case Histories of DSSs Uses Reported by Other Sources

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
Amine	2205	—	0.13 mole % H_2S, 0.9 mole % H_2O	237/115	87	CW with 600 to 1000 Cl, chromates inhib.	86/91	90	Started service in 1983
Amine	2205	304 SS	Amine, CO_2, cyanide, NH_3, H_2S, polysulphides	—	—	Steam	—	—	Delivered in 1987. U-bends. CS failed. Note 1
Amine	2205	2205 (F51)	Heating medium	284/212	309	Rich MDEA, CO_2	160/ 165	196	CO_2 removal plant, rich amine heater. seven years good service to date. Tubes see 13.7 fps. Expanded and strength welded
Crude	2205	CS	APS overhead	312/240	11	Undesalted crude feed	121/ 240 -series	417	Two bundles. Only bottom half
Crude	2205	CS	Wet naphtha (OH)	240/110 (from A/C)	8	CW	—	—	Two bundles
Crude	2205	—	Wastewater—1000 ppm maximum Cl, 5000 ppm maximum H_2S, ~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 15—Case Histories of DSSs Uses Reported by Other Sources (Continued)

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
Crude	2507	2507	Naphtha pump-around, water, chloride salts	—	—	CW	—	—	The tubes had extensive CSCC on the OD after approximately one year
Crude	2707	—	Crude overhead + H2S	350/300	35	Crude oil	100/140	350	—
Crude	2707	—	Atmospheric Overhead	280/113	10	Seawater	87/100	39	Original Al-Brass bundle fail due to acid dewpoint and corrosion under-deposits. Replacement in 2707 inspected after a year in service with no pitting or wall loss.
Crude	2707 twisted	—	Atmospheric OVHS	250/170	6	Crude	110/170	320	Original 2205 bundles failed after 12 months in service/ Upgraded 2707 bundle have a 5 year service life.
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 sulfur	A: 192/219 B: 205/255	—	Hydrocarbons, water, some chlorides	A: 302/ 219 B: 349/ 273	—	Ordered in 1984. CS lasted two years

Table 15—Case Histories of DSSs Uses Reported by Other Sources (Continued)

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
FCCU	2205	CS w/304L SS clad	Fractionator overhead	240[a]/100	5	CW	—	—	Eighteen bundles. Shell SS clad also on B, D, F
FCCU	2205	CS w/ Belzona	Cat gas	238/100	40	CW	—	—	Four bundles. 2205 installed in 6/98
FCCU	2205	—	Gas from FCC distillation	238/126	—	Treated water	68 to 99/201 to 220	—	Installed in 1988. CS lasted six years
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
Hydro-desulfurization	2205	—	BFW	221/390	—	Process gas	725/ 374		Ordered in 1985
Hydro-desulfurization	2205	—	Gasoil, H_2O, NH_4HS (30 %)	285/340	285	Steam	645/ 570	320	Installed 1987. CS lasted three years
Hydro-desulfurization (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 tmin of 0.050 in. (0.5 mpy to 0.7 mpy). Some tubes have been plugged.

Table 15—Case Histories of DSSs Uses Reported by Other Sources (Continued)

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
Hydroprocessing	2205	2205	Air	—	—	Reactor effluent	—	2300	SSC of multiple tube-to-tubesheet welds shortly after Jan. 2002 startup – some within 48 hours. Some welds confirmed to have high ferrite (see Reference 23).
Hydroprocessing	2205	2205	Air	—	—	Reactor effluent; 3.8 wt.% NH_4HS in sep.	—	1200	Nov. 2003 cracked pipe weld at REAC outlet; cracking within weld; weld hardness and ferrite were acceptable. 1.25 in. of pipe spring-back at failure location. Five years of service (see Reference 23).
Hydroprocessing	2205	2205	Air	—	—	Reactor effluent; 6 wt.% NH_4HS in sep.	—	2000	Mar. 2005 32 in. fracture in header box weld; explosion and fire. Cracking along fusion line. Some high ferrite and high hardnesses found in weld and HAZs; 9 years old (see Ref. 23)

Table 15—Case Histories of DSSs Uses Reported by Other Sources (Continued)

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
Hydroprocessing	2205	2205	Air	—	—	Reactor effluent; 7 wt.% NH_4HS in sep.	—	2300	June 2006 Multiple REAC outlet header and outlet piping weld cracks; some cracks within welds and some along fusion lines; some high ferrite at welds IDs; 2 years (see Ref. 23)
Hydroprocessing	2205	2205	Air	—	—	Reactor effluent; 6 wt.% NH_4HS in sep.	—	2050	Oct. 2009 Header box rupture during pressure test following repairs to cracked tube-to-tubesheet welds; cracking along fusion line. Weld ferrite and hardness all okay. Six years of service (see Ref. 23)

Table 15—Case Histories of DSSs Uses Reported by Other Sources (Continued)

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
Hydroprocessing	2205	2205	Air	—	—	Reactor effluent; 6 wt.% NH_4HS in sep.	—	2475	Sep. 2010 Leak in pipe-to-nozzle weld at REAC outlet; found by Inspector about to inspect weld for cracking; leak along fusion line; some zones of high ferrite found; 14 years of service (see Ref. 23)
Hydroprocessing	2205	2205	Air	—	—	Reactor effluent; 11.5 wt.% NH_4HS in sep.	—	1550	Mar. 2012 Multiple tube-to-tubesheet leaks during hydrotest after a turnaround heat exchanger cleaning and 8 years of service. New in 2004 and built with latest specifications (see Ref. 23)
Hydroprocessing	2205	2205	Air	—	—	Reactor effluent; mostly < = 5 wt.% NH_4HS in sep.	—	From 250 ~2000	15 additional REAC recently inspected for possible cracking with no failures to date (see Ref. 23)
HCN Hydrofiner	2205	CS	Hot separator overhead	300/115	227	CW	—	—	Two bundles
HCN Hydrofiner	2205	CS	Hot separator overhead	115/105	221	CW	—	—	—

Table 15—Case Histories of DSSs Uses Reported by Other Sources (Continued)

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
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

Table 15—Case Histories of DSSs Uses Reported by Other Sources (Continued)

Unit	Grade	Tube-sheet Material	Shell-side Service	Shell Temp. In/Out (°F)	Shell Pressure (psi)	Tube-side Service	Tube Temp. In/Out (°F)	Tube Pressure (psi)	Comments
SWS	2205	2205	Air	—	—	Stripper OH Condenser, high NH_4HS, 60 ppm Cl, non-detectable CN	Not reported	Not reported	Failed after one year due to NH_4HS corrosion over 3 ft of the second pass. Replaced with 825 which also failed in one year. Now replacing with Hastelloy C
SWS	2205 Piping (sch. 10)	—	—	—	—	Stripper OH Condenser, 15 %–22 % NH_4HS, 80–90 ppm CN	210	19	Initial failure after 4 years, and additional failures after 7 years. Pitting in HAZs and away from welds. Properly fabricated. Corrosion due to high CN and NH_4HS.
Amine	2507	—	DEA, H2S, residual water	150/115	140	Seawater	90/110	70	Original 2205 bundle failed pitting after 6 years. Upgraded bundle in 2507 has been in service for 10 years
Virgin Light Ends	2507	CS	Splitter overhead	111/100	205	CW	—	—	Sister bundle (A) is CS; CW corrosion

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

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

Table 16—Summary List of DSSs Refinery Applications to Date

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

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

[b] The high strength of DSS makes it difficult to bend in the field.

Annex A
(informative)

Example of Special Material Requirements for DSSs

NOTE 1 The requirements provided in Annex A are merely examples for illustration purposes only. They are not to be considered exclusive or exhaustive in nature. API makes no warranties, express or implied for reliance on or any omissions from the information contained in this document.

NOTE 2 The following two lists of typical production and fabrication requirements are of informative nature, and it is up to the end user to delineate the final requirements on their individual specifications for the procurement and sourcing of DSSs. This document is a technical report meant to summarize industry experiences for information sharing purposes.

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

A.1.1 Standard DSSs with ~22 % Cr shall be specified as UNS S32205 or as dual certified UNS S31803/ S32205. All other DSS grades can be ordered per the UNS number.

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

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

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

A.1.4 To ensure adequate corrosion resistance, each heat of material of standard DSS and super duplex grades (except for tubing and fasteners) shall be tested per Test Method B or Test Method C in ASTM A923, or as described in ISO 17781 and meet the acceptance criteria provided on the selected standard. The rapid screening test included in ASTM A923 shall not be used to accept material.

For lean DSS grades, each heat of material (except for tubing) shall be tested per ASTM A1084 Test Method B or Test Method C, or as described on ISO 17781 and meet the acceptance criteria provided on the selected standard. The rapid screening test included in ASTM A1084 shall not be used to accept material.

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

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

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

A.1.7 Solution annealing followed by quenching (e.g., water or gas quenching) is required after cold working on components (other than tubing) if the deformation exceeds 10 % for the lean or standard grades of DSS. All cold formed super DSS (other than tubing) shall be solution-annealed after cold forming.

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

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

A.2 Tubing

A.2.1 Tubing shall be seamless or welded. Welded tubing shall receive both hydrostatic testing and nondestructive electric (eddy current) testing in accordance with ASME SA-789; other testing methods in lieu of hydrostatic (i.e., air under water testing and pressure differential) may be accepted but must be approved by the purchaser. Tubing shall be manufactured from steel produced by the electric furnace process and subsequent vacuum oxygen decarburized (VOD) or argon oxygen decarburized (AOD). Secondary melting processes such as vacuum arc re-melt (VAR) and electro-slag re-melt (ESR) are permitted.

A.2.2 27 % Cr hyper DSS shall have a PREN greater than 48.

A.2.3 Tubing shall be solution-annealed in the corresponding temperature range listed in ASME SA-789 for that particular grade. The solution-annealing temperature should be held for sufficient time to eliminate intermetallic precipitates. Tubing shall then be rapid cooled by water, air, or reducing gas quenching to below 315 °C (600 °F). Tubes quenched using water or air shall be pickled after the annealing process. Tubes annealed in a controlled atmosphere (e.g., bright annealing) and quenched with a reducing gas (e.g., a combination of nitrogen and hydrogen) do not require pickling.

Heat treatments and quenching media other than the ones mentioned above require approval by purchaser.

A.2.4 Welded DSS tubing shall be bead worked prior to in-line solution annealing followed by rapid cooling unless otherwise approved by purchaser. Laser welded tubing can be annealed without prior bead working when approved by purchaser as long as it has proper root cleanliness and weld penetration (less than 0.004 in. or 6 % of specific wall thickness; see 6.2).

A.2.5 For standard, super, and hyper DSSs, either ASTM A923 Test Method C or corrosion testing per ISO 17781 shall be performed, and acceptance criteria of the selected specification must be met. If there is no acceptance criteria for the specific grade, then a criteria shall be agreed upon between the purchaser and producer.

A.2.6 For standard, super, and hyper DSSs, one specimen representing each heat lot shall receive a microstructural examination per the requirements of ASTM A-923 Test Method A or microstructural examination per ISO 17781. The presence of affected or centerline structures shall be grounds for rejection of the solution-annealed batch represented by the specimen, and the batch shall require reheat treatment and retesting. The sample size shall be a 2.54 cm (1 in.) long tube specimen for each heat lot.

A.2.7 For lean DSSs, ASTM A-1084 Test Method C shall be done and shall meet the required criteria.

A.2.8 No weld repairs to tubes are permitted.

A.2.9 Twisted tubes shall require solution annealing at the temperatures and cooling rates given in ASME SA-789.

A.2.10 Tubes and tube U-bends should typically not be heat treated after bending or straightening unless otherwise approved by purchaser. For standard grades, cold work shall be limited to 15 % maximum, which is equivalent to limiting U-bending bend radii to a minimum of 3.3 times the tube diameter (3.3D). For 25 % Cr and 27 % Cr DSS grades, bends can be made down to 2.0D bend radii with no heat treatment required. When heat treating is deemed necessary by the end user due to service environment, the following specification should be followed.

A.2.10.1 Prior to heat treatment, the tubes shall be cleaned with a solvent to remove lubricants and markings in the bent section.

A.2.10.2 The tube ID shall be purged with reducing gas to displace all oxygen in the tube ID before heat treatment begins, and such gas shall be maintained in the tube during the heat treatment to prevent oxidation of the ID surface.

A.2.10.3 The bends and 6 in. (150 mm) of the straight tube legs shall be electric resistance heated, consistent with the governing specification heat treatment (e.g., ASTM A789) and held for up to 30 seconds maximum. This shall be followed by rapid cooling to below 316 °C (600 °F).

A.2.10.4 The U-tube outside surface shall be free of heavy scaling. This may be accomplished by bright annealing, white pickling, or polishing with mineral belts. A light oxide on the outside surface of the heat treated tube is acceptable.

A.2.10.5 Two tube cross sections 25 mm (1 in.) long shall be tested in accordance with A.2.5 of this specification; one sample should be taken from the U-bend section and other another taken from the straight tube leg adjacent to the ER clamp location. This test shall be performed for each heat lot produced with the same bending and heat treatment procedure.

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

Annex B

(informative)

Example of Special Welding Procedure Qualification Requirements for DSSs

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

Annex C
(informative)

Example of Special Welding and Fabrication Requirements for DSSs

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

Annex D
(informative)

Example of a Duplex SS Casting Specification

The following list of typical production and fabrication requirements is of an informative nature, and it is up to the end user to delineate the final requirements on their individual specifications for the procurement and sourcing of DSSs. This document is a technical report meant to summarize industry experiences for information-sharing purposes.

D.1 General

D.1.1 Scope

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

D.1.2 Definitions

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

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

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

D.2 Process and Manufacture

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

a) electric arc or induction furnace melting followed by separate refining, such as VOD or AOD;

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

D.2.2 All castings furnished to this specification shall be solution-annealed at 1120 °C to 1150 °C (2050 °F to 2100 °F) for one hour per 25 mm (1 in.) section thickness, with a minimum of two hours and water quenched to room temperature to obtain the required duplex microstructure. The furnace to water quench time shall be less than one minute. Air cooling is not permitted.

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

D.3 Chemical Composition and Tests

D.3.1 Composition

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

D.3.2 Tension Testing

Supplementary requirement S14 from ASTM A703 shall be required.

D.4 Ferrite Content

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

D.4.2 The ferrite content shall be 35 % to 60 %. The ferrite content shall be determined by the manual point count in accordance with ASTM E562; minimum magnification shall be 200X. The maximum percent error per E562 shall be 10 %. Alternatively, a computerized microstructural analysis per ASTM E1245 or any other method previously agreed to in writing by the purchaser may be used.

D.5 Special Tests For Detrimental Intermetallic Phases

D.5.1 General

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

Table D.1—Impact Test and Corrosion Test Requirements for Castings with a Net Weight over 450 kg (1000 lb)

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

D.5.2 Corrosion Test

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

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

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

D.5.3 Impact Testing

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

D.5.3.2 The Charpy tests shall be performed consistently with the requirements and acceptance criteria listed on either ASTM A923, ASTM A1084, or ISO 17781.

D.6 Nondestructive Examination

D.6.1 General

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

D.6.1.2 For castings with a net weight over 450 kg (1000 lb), purchaser shall approve in writing the proposed procedures prior to nondestructive examination.

D.6.1.3 For castings with a net weight over 450 kg (1000 lb), all personnel performing nondestructive examinations (NDE) shall be certified in accordance with ASNT SNT-TC-1A. Personnel interpreting or evaluating results of nondestructive examination for acceptance or rejection shall be certified to SNT-TC-1A Level II or Level III.

D.6.1.4 Equipment shall meet the requirements of and be calibrated in accordance with ASME Code, Section V.

D.6.2 Visual Inspection

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

D.6.3 Liquid Penetrant Examination

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

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

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

D.6.4 Radiography

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

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

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

D.7 Repairs

D.7.1 Welding processes shall be SMAW or GTAW.

D.7.2 No autogenous welding is allowed.

D.7.3 Welding procedures (WPS and PQR) and welders shall be qualified per ASME Code, Section IX. Weld procedure qualification also needs to include impact testing. The Charpy tests shall be performed at consistently with the requirements and acceptance criteria listed on either ASTM A923, ASTM A1084, or ISO 17781.

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

Table D.2—Welding Consumables

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

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

D.8 Certification

D.8.1 The vendor shall certify in writing that the castings meet the requirements of the latest edition of ASTM A995 (including applicable supplementary requirements of ASTM A703) and this specification.

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

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

Annex E
(informative)

Example of Hot Isostatically Pressed (HIP) Duplex SS Material Specification

E.1 General

E.1.1 Scope

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

E.1.2 Definitions

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

Cross Contamination—Intermix of powder of different alloy type.

Filling Tube—Tube on top of capsule through which powder is filled.

Gas Atomization—Process in which a melt is slushed into small particles in a controlled chamber. When the particles solidify, a metal powder in which each particle has the same composition as the melt is formed.

QTC—Quality test coupon.

E.2 Material and Manufacture

E.2.1 Manufacturing Practice

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

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

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

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

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

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

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

E.2.2 Chemical Composition

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

E.2.3 Heat Treatment

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

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

E.3 Testing of Material Properties

E.3.1 Test Material

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

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

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

E.3.2 Microstructure

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

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

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

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

E.3.3 Mechanical Properties

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

E.3.3.2 Impact toughness shall be tested with Charpy-V notch testing, according to ASTM A370 on one set (including three specimens) of each test sample. The test temperature and acceptance criteria shall follow ISO 17781 guidance.

E.3.4 Corrosion Testing

Corrosion testing and acceptance criteria shall be per ISO 17781.

E.3.5 Densification

Argon level shall be tested with a gas chromatographic chemical analysis. The argon concentration shall be ≤ 0.05 ppm on materials atomized in nitrogen gas.

E.4 Nondestructive Testing

E.4.1 Ultrasonic Testing

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

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

E.4.2 Liquid Penetrant Testing

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

E.5 Finish and Appearance

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

E.6 Handling and Packing

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

E.7 Certification

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

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