

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](#).

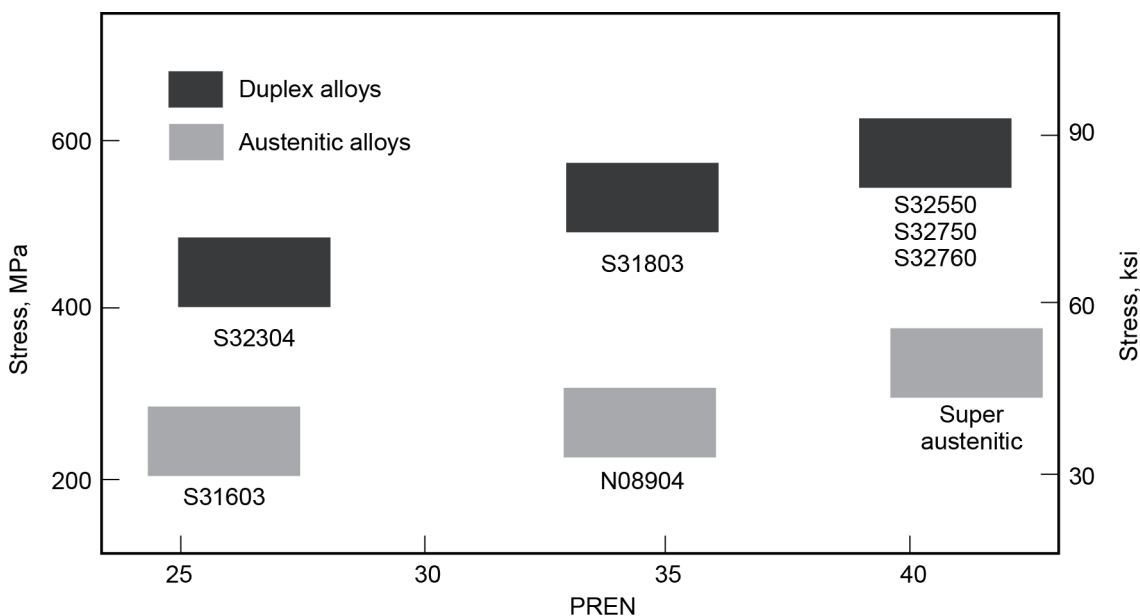


Figure 1—Comparison of the Proof Stress and Pitting Resistance (Based on PREN of the Bulk Chemistry) of Duplex and Austenitic SS ^[2]

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 (H₂S) 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

Mass % ^{a, e}												
UNS Number	Type ^b	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)

UNS Number	Type ^b	Mass % ^{a, e}										Other
		Cr	Mo	Ni	N	Cu	C	Mn	P	S	Si	
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, 48.0SPREN<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)

UNS Number	Type ^b	Cr	Mo	Ni	N	Mass % ^{a, e}						Si	S	P	Mn	C	Cu	6 % Mo Super Austenitic SS	Other
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](#)).

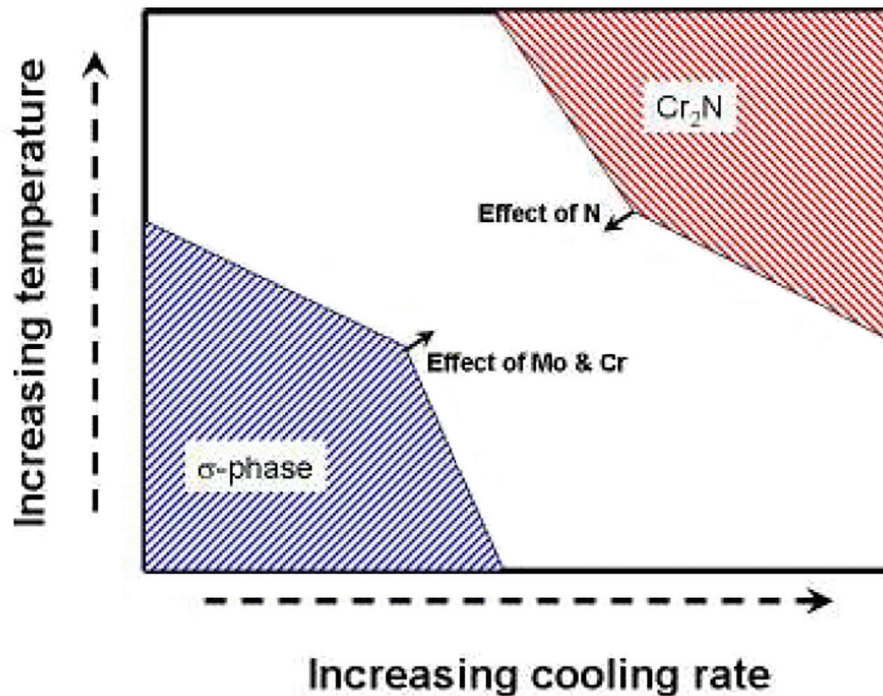


Figure 2—Schematic Diagram Showing the Conditions Under Which σ -Phase and Chromium Nitrides Are Formed in a Space Defined by Temperature and Cooling Rate. ^[43]

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](#)).

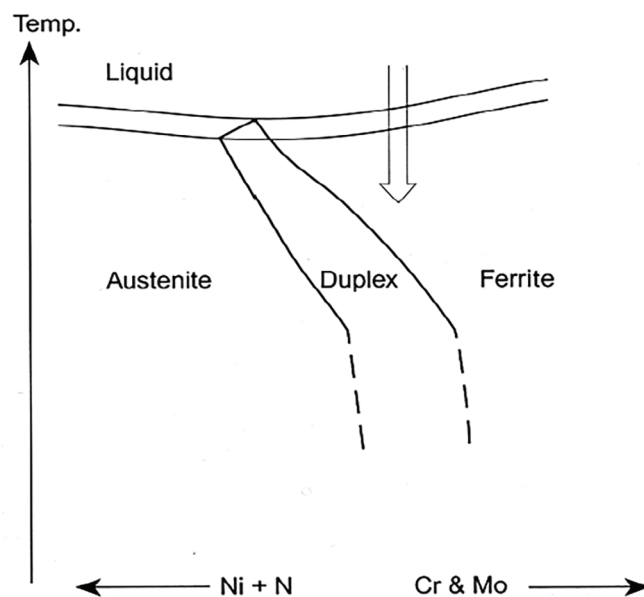


Figure 3—Solidification and Phase Development of Duplex Stainless Steels

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.

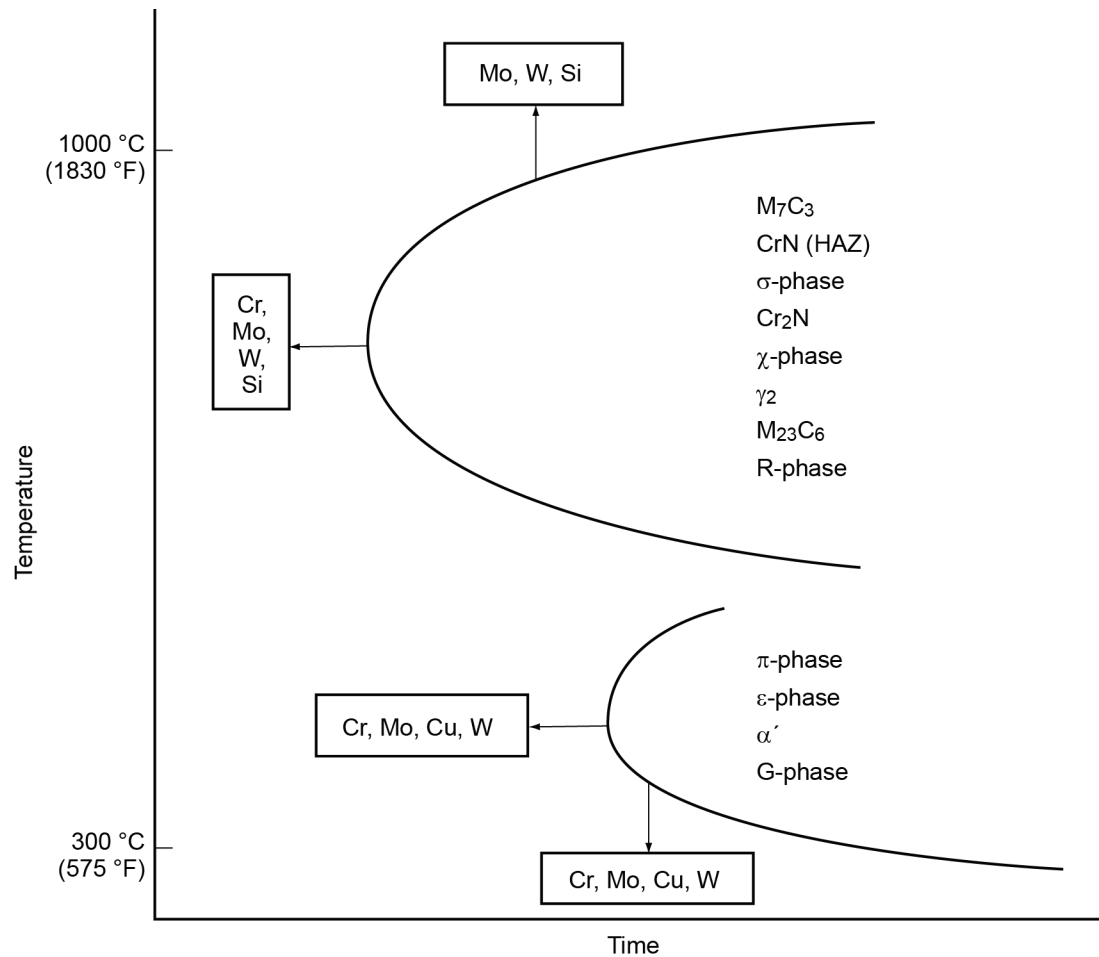
The addition of preheat is typically performed with great care to prevent elevated temperature exposure, and temperatures at the weldment should never exceed the maximum recommended interpass temperature for the specific grade. Excessive preheat and interpass temperatures will result in slow cool down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

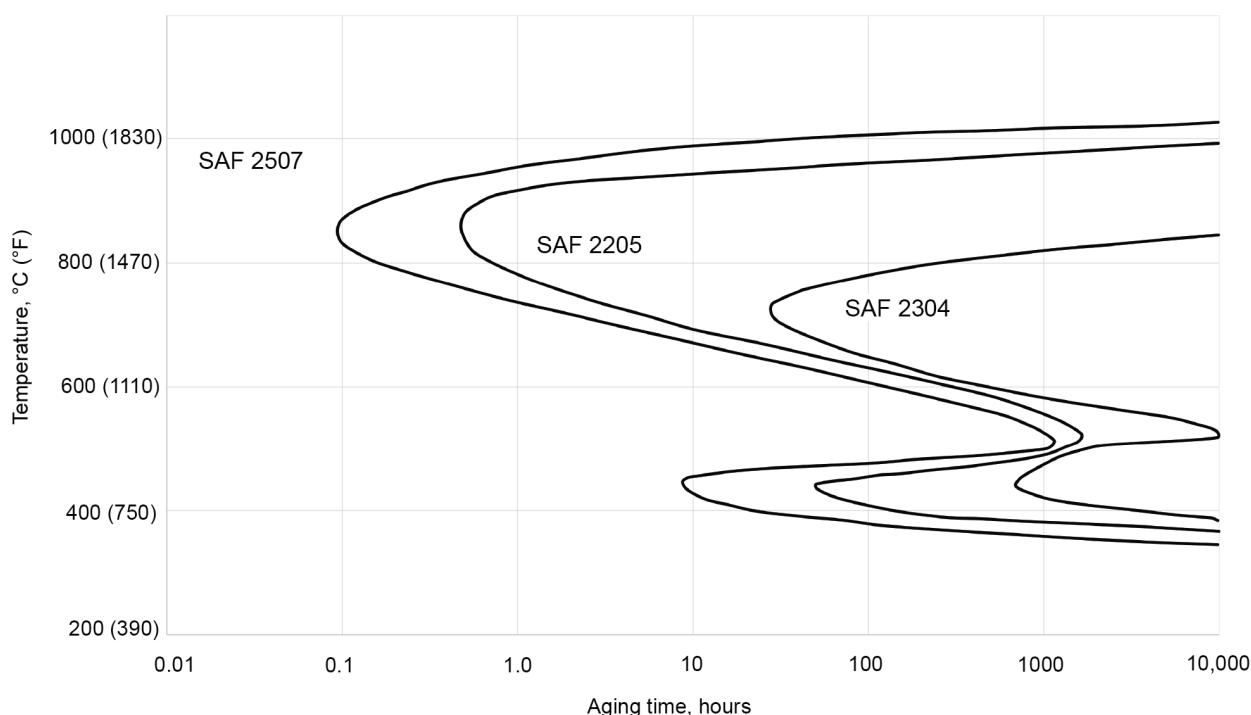
- for 22 % Cr DSSs with nitrogen >0.14 %, short exposure times (i.e., significantly less than one hour) to temperatures above 870 °C (1600 °F) will result in a significant loss of corrosion resistance and toughness;
- super and hyper DSSs show similar degradation after shorter exposure times (minutes) 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 $-51\text{ }^{\circ}\text{C}$ ($-60\text{ }^{\circ}\text{F}$) in the ASME B31.3 Code and $-29\text{ }^{\circ}\text{C}$ ($-20\text{ }^{\circ}\text{F}$) 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.

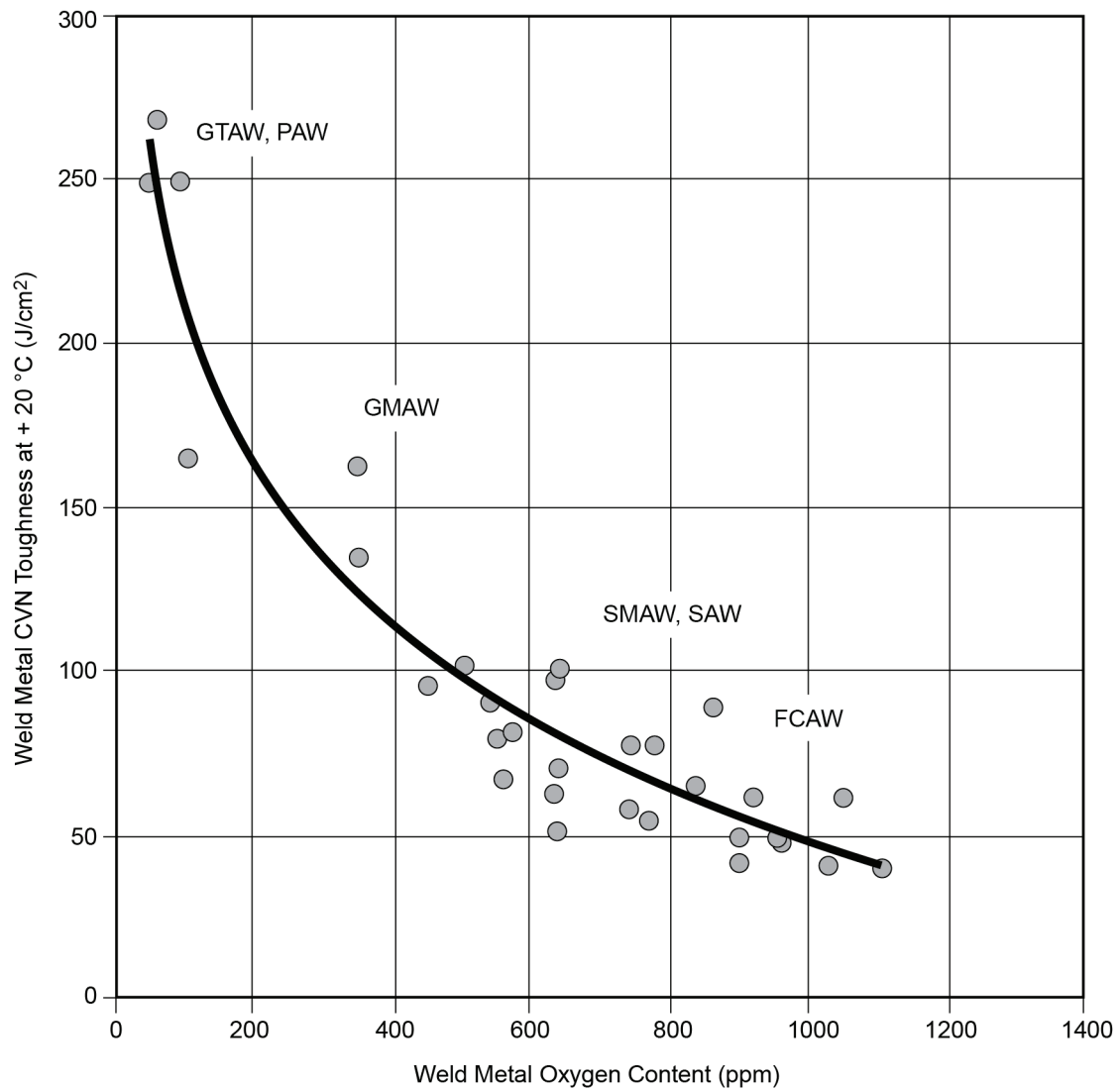


Figure 6—Effect of Weld Metal Oxygen Concentration on the Toughness of the Weld ^[7]