KNOWLEDGE
FOR A BRIGHTER
FUTURE

Practical guide to using duplex stainless steels

A GUIDE TO THE USE OF NICKEL-CONTAINING ALLOYS

Nickel INSTITUTE

knowledge for a brighter future

Practical guide to using duplex stainless steels

A GUIDE TO THE USE OF NICKEL-CONTAINING ALLOYS

Second Edition
Published 2020

Second Edition 2020 by Dr. James Fritz, edited by Geir Moe.
This edition is a major update of the first edition from 1990.

Cover photo: 2205 Duplex stainless steel tube-to-tubesheet weld, electrolytically etched with NaOH.

Practical guide to using duplex stainless steels

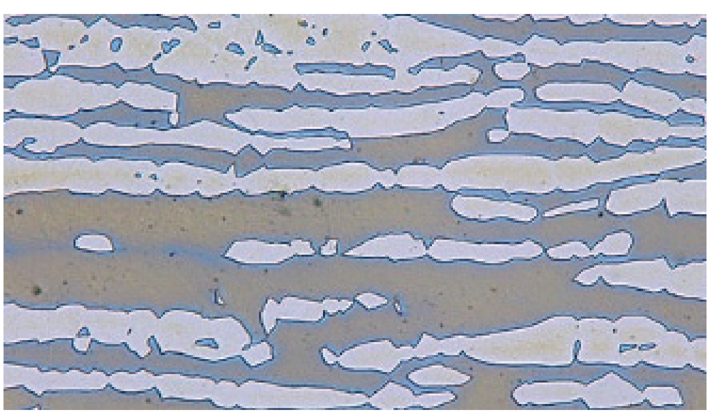
Introduction

While duplex is a frequently used term with many different meanings, the term *duplex stainless steel* has come to mean a grade whose annealed structure is typically about equal parts austenite and ferrite, *Figure 1*. Although not formally defined, it is generally accepted that the lesser phase will be at least 30% by volume. For an in-depth discussion of the microstructures of duplex stainless steels see reference (1).

Duplex stainless steels offer several advantages over the common austenitic stainless steels. The duplex grades are:

- highly resistant to chloride stress corrosion cracking;
- about twice as strong as the common austenitic stainless steels, which allows for weight savings by means of higher allowable stresses and thinner material and thus cost savings;
- substantially lower in nickel content than common austenitic grades, and thus are less sensitive to nickel price.

Figure 1 Wrought UR 52N+ (UNS S32520) duplex stainless steel plate in the mill-annealed and water–quenched condition. The microstructure contains approximately equal amounts of flattened islands of austenite (light phase) and ferrite (dark phase). NaOH etchant/ Magnification 1000X. (courtesy of Materials Technology Institute, Inc.)



In recent years economic pressure due to the high price of nickel and molybdenum has increased the interest in duplex stainless steels as lower cost alternatives to austenitic stainless steels. The duplex family of stainless steels offer a wide range of pitting and crevice corrosion resistance from the *lean* duplex grades with resistance that approaches Type 316L (S31603) austenitic stainless steel to *hyper* duplex grades that are more resistant than the 6%Mo super austenitic stainless steels.

First and second-generation duplex stainless steels

Duplex stainless steels have been available since the 1930s. Because of their relatively high chromium and molybdenum contents, the first-generation duplex stainless steels, such as Type 329 (S32900) and Uranus 50 (S32404), have good localised corrosion resistance. However, when welded these grades lose the optimal balance of austenite and ferrite and consequently, the corrosion resistance and toughness are reduced. Although these properties can be restored by a post weld heat treatment, most applications of first-generation duplex stainless steels were restricted to the annealed condition without subsequent welding.

In the 1970s this problem was overcome through the use of nitrogen as an alloy addition. The introduction of Argon-Oxygen Decarburisation (AOD) technology permitted the precise and economical control of nitrogen content in stainless steel. Although nitrogen was initially used because it was an inexpensive austenite former, replacing some nickel, it was soon discovered that it had other benefits including improved tensile properties, rapid restoration of the desired phase balance after welding, and increased localised corrosion resistance.

Increased nitrogen content causes the ferrite-to-austenite transition to occur at higher temperatures, allowing the formation of an acceptable balance of austenite and ferrite after a rapid thermal cycle such as that in the heat-affected zone (HAZ) of a weld. This nitrogen advantage enables the use of duplex stainless steels in the as-welded condition and spurred the development of second-generation duplex stainless steels. Second-generation duplex grades are best defined by a required nitrogen addition typically in the range of 0.15 – 0.40%.

Table 1 Nominal compositions (wt%) of wrought duplex stainless steels

UNS designation	Common name or type	EN	Cr	Mo	Ni	Cu	Mn[A]	C[A]	N[A]	Other	PRE[B]
First-generation duplex stainless steels											
S31500		1.4424	18.5	2.7	4.9	-	1.2-2.0	0.03	0.05-0.10	1.7Si	27
S32404			21	2.2	6	1.4	2.0	0.04	-	-	28
S32900	329[C]	1.4480	26	1.5	4.5	-	1.0	0.08	-	-	31
Second-generation duplex stainless steels											
“Lean” duplex											
S32001		1.4482	20	0.6	1.6	-	4.0-6.0	0.03	0.05-0.17	-	22
S32101		1.4162	21	0.4	1.5	0.5	4.0-6.0	0.04	0.20-0.25	-	26
S32202		1.4062	22.5	0.4	2.2	-	2.0	0.03	0.18-0.26	-	27
S32304	2304[D]	1.4362	23	0.3	4.0	0.3	2.5	0.03	0.05-0.20	-	26
S82011			21	0.4	1.5	-	2.0-3.0	0.03	0.15-0.27	-	26
S82012		1.4635	19.5	0.3	1.2	-	2.0-4.0	0.05	0.16-0.26	-	25
S82013			20	-	1	0.8	2.5-3.5	0.06	0.20-0.30	-	24
S82122			21	0.6	2	1	2.0-4.0	0.03	0.15-0.20	-	25
		1.4655	22.5	0.3	4.5	2	2.0	0.03	0.05-0.20	-	26
		1.4669	22	0.5	2	2.2	1.0-3.0	0.045	0.12-0.20	-	26
Molybdenum-containing “lean” duplex											
S32003			21.5	1.8	3.3	-	2.0	0.03	0.14-0.20	-	30
S81921			21	1.5	3		2.0-4.0	0.03	0.14-0.20	-	27
S82031		1.4637	21	1	3		2.5	0.05	0.14-0.24	-	27
S82121			21.5	0.8	3		1.0-2.5	0.035	0.15-0.25	-	27
S82441		1.4662	23.5	1.5	3.5		2.5-4.0	0.03	0.20-0.30	-	33
“Standard” duplex											
S31803	2205[D]	1.4462	21	2.7	5.0	-	2.0	0.03	0.08-0.20	-	31
S32205	2205[D]	1.4462	22	3	5.0	-	2.0	0.03	0.14-0.20	-	35
S31200		1.4460	25	1.7	6.0	-	2.0	0.03	0.14-0.20	-	32
S32950			26.5	1.5	4.8	-	2.0	0.03	0.15-0.35	-	34
S31260		1.4481	25	3	7	0.5	1.0	0.03	0.10-0.30	0.3W	37
S32808			27	1	7	-	1.1	0.03	0.30-0.40	2.3W	39
“Super” duplex											
S32506			25	3	6	-	1.0	0.03	0.08-0.20	0.15W	40
S32520		1.4507	25	4	6.5	1	1.5	0.03	0.20-0.35	-	41
S32550	255[D]	1.4507	25	3.5	6	2	1.5	0.04	0.10-0.25	-	40
S32750	2507[D]	1.4410	25	4	7	-	1.2	0.03	0.24-0.32	-	42
S32760	Z100[D]	1.4501	25	3.5	7	0.7	1.0	0.03	0.20-0.30	0.7W	41
S32906		1.4477	28	2	6	-	0.80-1.5	0.03	0.30-0.40	-	40
S39274			25	3	7	0.5	1.0	0.03	0.24-0.32	1.8W	42
S39277			25	3.5	7	1.5	0.80	0.025	0.23-0.33	1W	

“Hyper” duplex											
S32707		1.4658	27	4.8	6.5	-	1.5	0.03	0.30-0.50	1.0Co	50
S33207		1.4485	30	3.5	7	-	1.5	0.03	0.40-0.60	-	52
Austenitic stainless steels											
S30403	304L[C]	1.4307	18	-	8	-	2.0	0.03	0.10	-	20
S31603	316L[C]	1.4404	16	2	11	-	2.0	0.03	0.10	-	24
S31703	317L[C]	1.4438	18	3	11	-	2.0	0.03	0.10	-	29
N08904	904L[D]	1.4539	20	4.1	24	1.0	2.0	0.02	-	-	34
N08367			20	6	24	-	2.0	0.03	0.18-0.25	-	43
S31254		1.4547	20	6	18	0.8	1.0	0.02	0.18-0.22	-	43

[A] ASTM Specification range or maximum if single number
[B] Pitting Resistance Equivalent number calculated from PRE = %Cr + 3.3[%Mo + 0.5(%W)] +16(%N) and the nominal compositions
[C] A grade designation originally assigned by American Iron and Steel Institute (AISI)
[D] Common name, not a trademark, widely used, not associated with any one producer

Categories of duplex stainless steel

Wrought duplex stainless steels

Table 1 lists the compositions of some of the more common wrought duplex stainless steels with some selected austenitic stainless steels included for comparison. Also tabulated in this table are the Pitting Resistance Equivalent numbers (PRE) calculated from the following expression and each alloy’s nominal composition:

PRE = % Cr + 3.3[%Mo + 0.5(W)] + 16[%N]

This empirical relationship, derived by statistical regression applied to a large volume of corrosion test results, provides a relative ranking of a stainless steel’s pitting and crevice corrosion resistance based on the levels of Cr, Mo, W, and N present in the alloy. The names, trademarks, registered trademarks and the associated producers for common wrought duplex stainless steels are listed in *Table 2*.

The second-generation grades are loosely divided into categories depending on the level of alloying. *Lean* duplex stainless steels are characterised by having relatively low levels of nickel and/or molybdenum. To compensate for the reduced Ni, which is a strong austenite former, the N and Mn levels are increased to provide an acceptable balance of austenite and ferrite. As a group, the lean duplex stainless steels have a very good combination of strength and corrosion resistance and are ideally suited for structural applications, tank construction, and service environments that require resistance to chloride stress corrosion cracking.

The *standard* duplex stainless steel grades typically contain 22 to 25% Cr and 2 to 3% molybdenum. Grades in this category are used widely across all industry sectors. Type 2205 (S32205) duplex stainless steel has evolved into the workhorse grade and is by far the most widely used of all second-generation duplex stainless steels. With many producers in Europe, North America, and Asia, it is readily available in almost all product forms.

There currently are two variations of the 2205 grade listed in ASTM A240, S31803 and S32205. The S32205 grade has slightly higher levels of Cr, Mo, and N, essentially the upper half of the ranges permitted for these elements in S31803. It was developed to address the potential loss of corrosion and toughness properties in the HAZ of fabrication welds produced in S31803. It is recommended that users specify the S32205 grade and fortunately it is by far the most commonly available. If product specifications mandate the use of the S31803 designation, users should require that all S31803 products have a composition that also meets requirements for the S32205 designation to obtain the expected consistency of properties.

The *super* duplex stainless steels typically have levels of Cr, Mo, and N (and W when used) sufficient to provide a PRE number that is approximately 40 or higher. These grades are roughly equal to the 6%Mo super austenitic grades in their resistance to localised chloride attack and they are often used for applications that involve seawater exposure, chemical process, pollution control, acid leach mining and other industries with arduous environments.

The S32707 and S33207 hyper duplex stainless steels are more highly alloyed than super duplex and are designed for aggres-

Table 2 Common names, trademarks, registered trademarks, and associated stainless steel producers of duplex stainless steel		
Producer	**Names, trademarks & registered trademarks**	**UNS designation**
AK Steel	Nitronic® 19D*	S32001
ArcelorMittal - Industeel	UR 2202	S32202
ArcelorMittal - Industeel	UR 35N	S32304
ArcelorMittal - Industeel	UR 45N	S31803
ArcelorMittal - Industeel	UR 45N+	S32205
ArcelorMittal - Industeel	UR 45NMo	S32205
ArcelorMittal - Industeel	UR 47N	S32750
ArcelorMittal - Industeel	UR 52N	S32550
ArcelorMittal - Industeel	UR 52N+	S32520
ArcelorMittal - Industeel	UR 76N	S32760
ATI Allegheny Ludlum	AL 2003™	S32003
ATI Allegheny Ludlum	AL 2205™	S32205
Carpenter Technology	7-Mo PLUS®	S32950
Langley Alloys	Ferralium® 255	S32550
Outokumpu	LDX 2101®	S32101
Outokumpu	2205 Code Plus Two®	S32205
Outokumpu	SAF 2507	S32750
Sandvik	3RE60	S31500
Sandvik	SAF 2304	S32304
Sandvik	SAF 2205	S32205
Sandvik	SAF 2507	S32750
Sandvik	SAF 2707 HD	S32707
Sandvik	SAF 3207 HD	S33207
Sumitomo Metal Technology, Inc.	DP-3	S31260
Sumitomo Metal Technology, Inc.	DP-3W	S39274
Sumitomo Metal Technology, Inc.	DP-28W	S32808
Thyssen Krupp	Nirosta® 4462	S32205
Thyssen Krupp	Nirosta® 4501	S32760
Rolled Alloys	Zeron® 100	S32760

sive acidic and chloride-containing environments. Because these grades are more highly alloyed than the super duplex stainless steels, the term *hyper* duplex stainless steel is sometimes used to describe this category of alloy and to distinguish it from the super duplex grades. The hyper grades are currently only available as seamless pipe and tubing because of the difficulty in heat treatment and avoiding deleterious intermetallic particles, and it remains to be seen if other product forms and other similar competitive grades will be developed.

Cast duplex stainless steels

First generation cast duplex stainless steels such as CD4MCu (J93370) have been used for more than fifty years. There are now various second-generation cast grades, such as CD4MCuN (J93372) and CD3MWCuN (J93380), that offer improved weldability and corrosion resistance in comparison to the lower nitrogen containing first generation grades, *Table 3*. As shown in *Figure 2*, the solution annealed microstructure of cast duplex stainless steel also contains approximately equal amounts of austenite and ferrite.

Table 3 Designations and specifications for duplex stainless steel castings			
ACI or other names	**UNS number**	**ASTM**	**PREN [A]**
CD4MCu, 1A	J93370	A890	31
CD4MCuN, 1B	J93372	A890/A995	34
CD3MCuN	J93373	A890	40
CE8MN, 2A	J93345	A890/A995	37
CD6MN, 3A	J93371	A890/A995	35
CD3MN, 4A	J92205	A890/A995	35
CE3MN, 5A	J93404	A890/A995	41
CD3MWCuN, 6A	J93380	A890/A995	41

[A] Pitting Resistance Equivalent number calculated from PRE = %Cr + 3.3[%Mo + 0.5(%W)] +16(%N) and the nominal compositions

The second-generation cast duplex stainless steels provide good corrosion resistance, excellent resistance to stress corrosion cracking, and improved strength over the cast 300-series austenitic stainless steels. The ferrite portion of the microstructure has a high solubility for sulphur and phosphorus so their propensity toward solidification cracking is much lower than austenitic stainless steel castings of similar corrosion resistance. Duplex stainless steel castings have been used extensively by pump and valve industries supplying products in to a wide range of industrial applications.

Mechanical and physical properties

Duplex stainless steels characteristically are stronger than either of their two phases considered separately. The duplex grades have yield strengths twice those of the common austenitic grades while retaining good ductility, *Table 4*. In the annealed condition, the duplex grades have outstanding toughness and with the second-generation duplex grades, it is possible to retain toughness and corrosion resistance after welding.

The high strength of these steels is reflected in a correspondingly high fatigue strength and these steels have a long history in rotating equipment applications. Their behavior in fatigue is like that of a ferritic steel in that they exhibit a fixed fatigue limit. Similarly, it has been found that fatigue design rules for structural steels can be applied to duplex stainless steels of the same strength level.

The physical properties such as coefficient of thermal expansion and the heat-transfer characteristics of the duplex stainless steels are intermediate to those of the ferritic and the austenitic stainless steels.

Corrosion resistance

Pitting and crevice corrosion

Duplex stainless steels comprise a family of grades with a wide range of corrosion resistance. They typically have higher chromium contents than the standard austenitic grades and have a molybdenum content that can vary from a fraction of a percent for some of the lean grades to greater than 6.5 % for the S32707 hyper grade. As demonstrated by the critical pitting and crevice corrosion temperatures presented in *Figures 3* and *4*, the resistance of duplex stainless steels to localised chloride attack covers a very wide range and is proportional to the PRE number of the specific grade.

For the lower range of corrosion resistance there are the lean duplex grades such as S32001, S32101, and S32202 which have a pitting and crevice corrosion resistance that is superior to that of Type 304L (S30403) austenitic stainless steel and approaches that of Type 316L. In the mid-range are the standard grades such as Type 2205, which have a pitting resistance about equal to that of Type 904L (N08904) austenitic stainless steel. On the high end of corrosion resistance are the super duplex stainless steels which have a

Figure 2 Solution annealed cast CD3MWCuN (UNS J93380) microstructure with isolated islands of austenite (light phase) in a ferrite matrix (dark phase). NaOH etchant/Magnification 400X. (courtesy of Materials Technology Institute, Inc.)

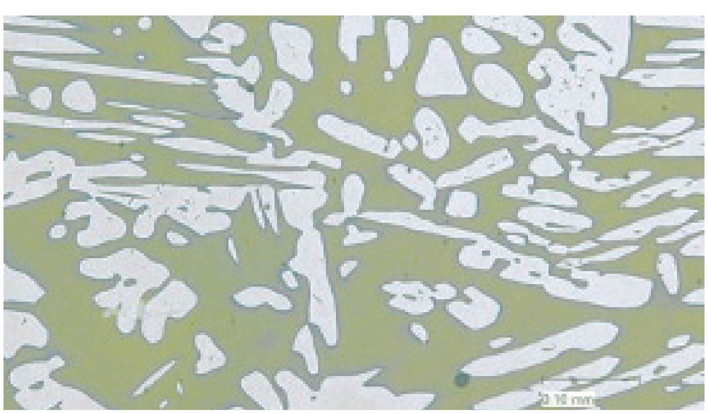


Figure 3 Critical pitting and critical crevice corrosion temperatures for various duplex and austenitic stainless steel. Measurements made using ASTM G48 Test methods A and B (results from reference (2) and producers' data).

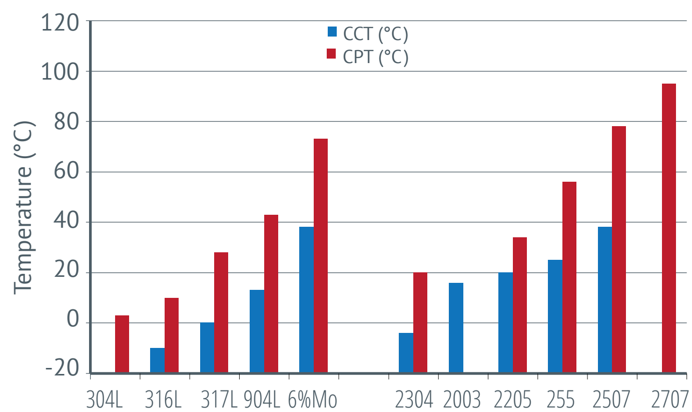


Figure 4 Plot of the ASTM G150 critical pitting temperature vs. the PRE number. (plotted with data from producers' and reference (4)).

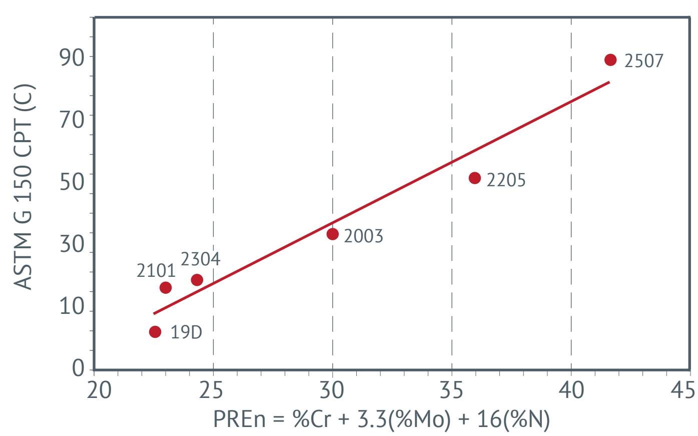


Table 4 Mechanical properties of wrought duplex stainless steels based on the minimum ASTM A240 requirements									
Common name or type	UNS number	EN	0.2% Yield strength (min.)		Tensile strength (min.)		Elongation (min.)	Hardness (max.)	
			MPa	ksi	MPa	ksi	%	Brinell	Rockwell C
Duplex stainless steels									
	S31200	1.4460	450	65	690	100	25	293	31
	S31260		485	70	690	100	20	290	-
	S31803		450	65	620	90	25	293	31
	S32001		450	65	620	90	25	-	25
	S32003		485[A] 450[B]	70 65	690 655	100 95	25 25	293 293	31 31
	S32101	1.4162	530[A] 450[B]	77 65	700 650	101 94	30 30	290 290	31 31
	S32202	1.4062	450	65	650	94	30	290	31
2205	S32205	1.4462	450	65	620	90	25	293	31
2304	S32304	1.4362	400	58	600	87	25	290	32
	S32506		450	65	620	90	18	302	32
	S32520	1.4507	550	80	770	112	25	310	32
255	S32550	1.4507	550	80	760	110	15	302	32
2507	S32750	1.4410	550	80	795	116	15	310	32
Z100	S32760	1.4501	550	80	750	108	25	310	32
	S32808		500	72	700	101	15	310	32
329	S32900	1.4480	485	70	620	90	15	269	28
	S32906		650[C] 550[D]	94 80	800 750	116 109	25 25	310 310	32 32
	S32950		485	70	690	100	15	293	32
	S39274		550	80	800	116	15	310	32
	S81921		450	65	620	90	25	293	31
	S82011		450[B]	65	655	95	30	293	31
	S82012		500[A] 400[B]	73 58	700 650	102 94	35 35	- 293	31 -
	S82013		450	65	620	90	30	293	31
	S82031		500[A] 400[B]	73 58	700 650	102 94	35 35	- 290	31 -
	S82121		450	65	650	94	25	286	30
	S82122		500[E] 400[F]	72 58	700 600	101 87	25 30	290 290	32 32
	S82441		540[C] 480[D]	78 70	740 680	107 99	25 25	290 290	31 31
Austenitic stainless steels									
304L	S30403	1.4307	170	25	485	70	40	201	92[I]
316L	S31603	1.4404	170	25	485	70	40	217	95[I]
317L	S31703	1.4438	205	30	550	75	40	217	95[I]
904L	N08904	1.4539	220	31	490	71	35	-	90[I]
6%Mo	N08367		310[G] 310[H]	45 45	690 655	100 95	30 30	- 241	100[I] -
6%Mo	S31254	1.4547	310[G] 310[H]	45 45	690 655	100 95	35 35	223 223	96[I] 96[I]

[A] For thicknesses ⩽ 0.187 inches [5.00 mm]
[B] For thicknesses > 0.187 inches [5.00 mm]
[C] For thicknesses < 0.4 inches [10.00 mm]
[D] For thicknesses ⩾ 0.4 inches [10.00 mm]
[E] For thicknesses ⩽ 0.118 inches [3.00 mm]
[F] For thicknesses > 0.118 inches [3.00 mm]
[G] Sheet and Strip
[H] Plate
[I] Rockwell B Scale

pitting and crevice corrosion resistance similar to the 6% Mo super austenitic grades and the newly developed and more resistant hyper duplex grades, which approach the pitting resistance of the Ni-Cr-Mo alloy, C276 (N10276).

Resistance to chemical environments

The different levels of chromium, molybdenum, and nickel in second-generation duplex stainless steels result in different levels of resistance to chemical environments. The corrosion data presented in *Table 5* show that depending on the specific duplex grade and the chemical environment, duplex stainless steels compare favourably with austenitic grades in their resistance. When selecting a stainless steel for aggressive chemical environments it is recommended that a corrosion specialist be consulted to ensure that appropriate candidate grades are considered. Many common industrial environments and suitable grades are reviewed in item 1 of Additional Resources.

Chloride stress corrosion cracking

One of the primary reasons for using duplex stainless steels is their excellent resistance to chloride stress corrosion cracking (SCC). However, duplex stainless steels are not immune to chloride SCC and sufficiently high temperatures and chloride contents can produce cracking. For example, all duplex and austenitic stainless steels are susceptible to SCC in concentrated boiling magnesium chloride solutions, *Figure 5*. Fortunately, this test is so severe that it is not representative of most practical environments and its results are not a reliable indication of chloride SCC susceptibility in typical heat transfer applications with less concentrated chlorides, usually derived from sodium chloride.

Less aggressive tests, such as immersion testing in boiling NaCl and $CaCl_2$ solutions and the various "Wick Tests" with NaCl solutions have been shown to correlate with field experience, though cannot be used to determine resistance for specific applications.[2] Based on results from these tests[3] all duplex stainless steels have a very good resistance to chloride SCC and are comparable to alloy 20 and the 6% molybdenum super austenitic grades. The cracking thresholds for various

Table 5 Corrosion rates in select chemical environments*

Solution, Temperature	Corrosion rate – mpy (mm/y)							
	Type 304L (S30403)	Type 316L (S31603)	Type 317L (S31703)	(S32101)	(S32003)	2205 (S32205)	255 (S32550)	2507 (S32750)
1% Hydrochloric acid, Boiling	85 (2.28)	59.0 (1.50)	56.3 (1.43)	-	48.0 (1.22)	12.2 (0.31)	-	3 (0.076)
10% Sulfuric acid, Boiling	662 (16.81)	635 (16.13)	294 (7.49)	-	259 (6.57)	207 (5.26)	40 (1.02)	-
20% Phosphoric acid, Boiling	< 1.0 (< 0.03)	0.2 (<0.01)	0.7 (0.02)	-	0.39 (0.01)	0.8 (0.02)	-	-
10% Sulfamic acid, Boiling	50 (1.3)	124 (3.16)	83.1 (2.11)	-	11.4 0.29	21.2 0.54	-	-
65% Nitric acid, Boiling	8.9 (0.23)	22.3 (0.27)	48.4 (1.23)	2.7 (0.07)	30.7 (0.78)	20.6 (0.52)	16 (0.41)	16 (0.41)
20% Acetic acid, Boiling	0.1 (0.003)	0.12 (0.003)	0.48 (0.012)	-	0.00 (0.000)	0.1 0.002	-	
80% Acetic acid, Boiling	-	-	-	0.08 (0.002)	-	0.1 (0.003)	<0.1 (<0.003)	0.8 (0.020)
45% Formic acid, Boiling	-	23.4 (0.59)	18.3 (0.46)		15.0 (0.38)	0.5 (0.01)	-	-
10% Oxalic acid, Boiling	-	48.4 (1.23)	46.8 (1.19)	62.2 (1.58)	7.1 (0.18)	5.1 (0.13)	-	-
50% Sodium hydroxide, Boiling	71 (1.80)	77.6 (1.97)	32.8 (0.83)	-	-	23.9 (0.61)	7.6 (0.05)	-

* Data from producers and MTI Publication No. 47, *Corrosion Testing of Iron- and Nickel-Based Alloys*

duplex stainless steels under fully immersed conditions in neutral salt solutions are shown in *Figure 6*.

Metallurgy of duplex stainless steels

Understanding the metallurgy of the duplex grades is necessary to understand the welding practices required to ensure tough and corrosion-resistant fabrications. In order to maintain acceptable corrosion resistance and toughness, a desirable austenite–ferrite balance must be achieved, and undesirable secondary phases must be avoided. Detrimental secondary phases include intermetallic compounds such as *sigma* and *chi* phase, undesirable carbide and nitride formation, and precipitation of alpha prime. The composition of duplex stainless steels and their processing, including fabrication practice, must ensure adequate formation of austenite to achieve a desirable austenite-ferrite balance and avoid the formation of undesirable secondary phases.

Austenite/ferrite balance

As shown in the phase diagram in *Figure 7*, duplex stainless steels solidify as 100% ferrite (α) and upon subsequent cooling will reach a temperature where some of the ferrite transforms to austenite (γ). The temperature for the α to γ transition will depend on the alloy composition and typically occurs in the range of 1200 to 1400 °C (2200 to 2550 °F). As the temperature drops below the α to γ transition temperature there is an increase in the equilibrium amount of austenite down to about 1000 °C (1832 °F). Below this temperature there is little change in the equilibrium austenite-ferrite balance.

If a duplex grade is cooled too rapidly, a condition that can occur with low heat input welds on large pieces, there may be insufficient time for the austenite to form resulting in a structure that is enriched in ferrite. *Figure 7* shows that increased nitrogen content moves the α to γ transition to higher temperatures where the rate of transition is faster

Figure 5 SEM micrograph showing cracking on S32750 specimens after 24 hours in 45% $MgCl_2$ at 155°C

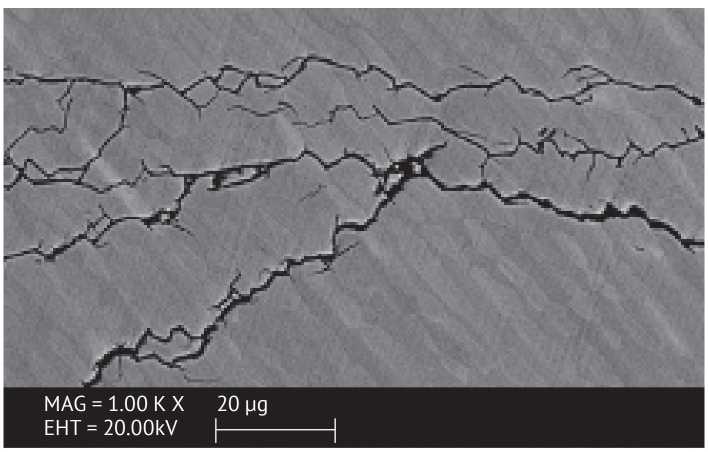


Figure 6 The chloride SCC threshold for various duplex and select austenitic stainless steels in neutral chloride solutions. (Courtesy of Sandvik)

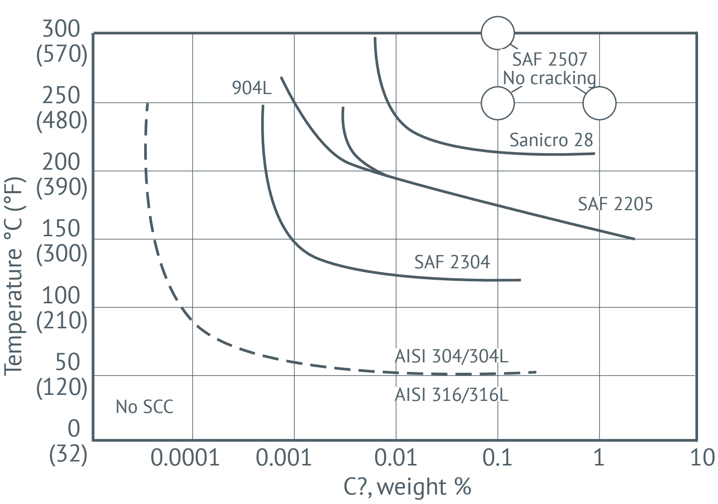
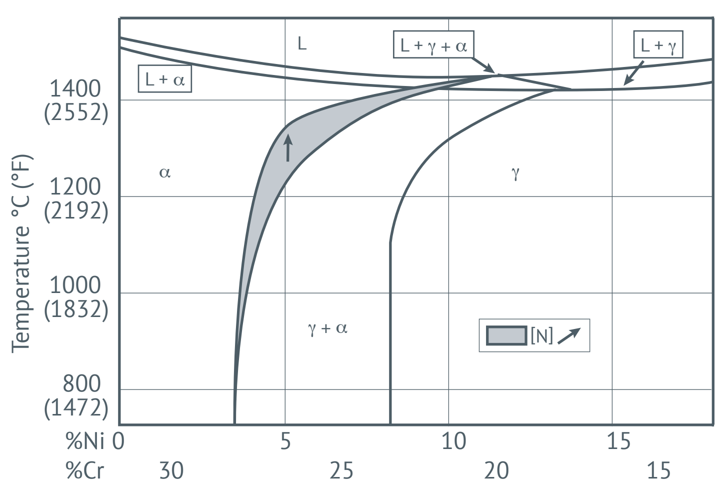


Figure 7 Nickel - Chromium phase diagram for a 68% iron duplex stainless steel, showing the influence of increased nitrogen content on the ferrite to austenite transition temperature. (from reference 4)



making it more likely to achieve an acceptable austenite-ferrite balance. With second-generation duplex stainless steels and properly qualified fabrication procedures, the problem of too much ferrite can usually be avoided. Duplex welding filler metals are over-alloyed with nickel to promote austenite formation during cooling.

The increased level of ferrite that occurs upon heating to high temperatures can be useful in hot rolling or forging where the weak ferrite phase facilitates production. If the steel cools sufficiently during hot rolling so that a substantial amount of austenite forms, further deformation can produce cracking, sometimes very serious, because of the mismatch in high-temperature strengths of the austenite and ferrite phases.

If ease of production were the only consideration, then the duplex grades would be low in nitrogen and balanced to ensure that the steel remains ferritic during hot rolling. However, the interests of the fabricator and the user are opposite those of the producer in that the user wants rapid austenite formation to ensure toughness and restore corrosion resistance. If the fabricator welds a low-nitrogen duplex grade with a rapid quench of the HAZ (following what would be a good practice for austenitic stainless steel grades), then it is possible for this region to be excessively ferritic and lacking in toughness and corrosion resistance.

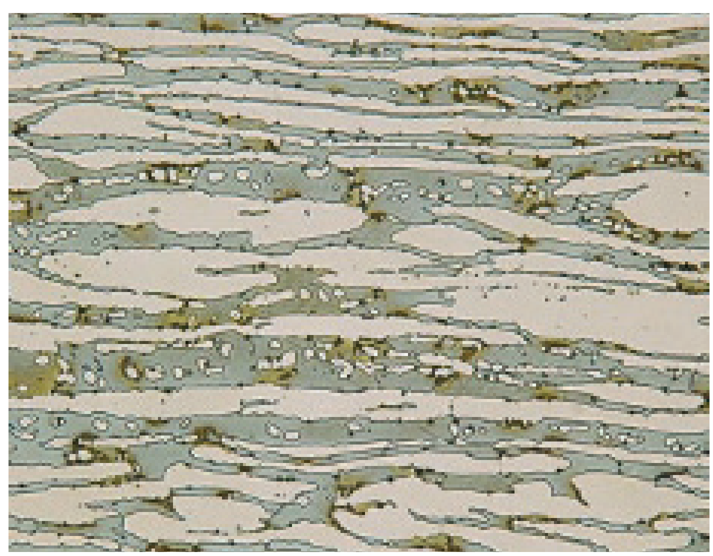
Although there is no single defined limit on ferrite content, any level greater than approximately 70% (ISO 17781) would be considered unacceptable for most applications. A more restrictive limit for ferrite content should be imposed by the user when qualifying weld procedures in critical applications, especially those with substantial safety risks, those involving hydrogen sulphide and those exposed to low operating temperatures. For guidance on the measurement of the ferrite content of duplex stainless steels see reference (6).

Undesirable secondary phases

A potentially more serious problem, particularly because of its influence on toughness and corrosion properties, is the effect of temperature excursions into a range where undesirable secondary phases can form. The specific undesirable phases and the critical temperature range for their formation will depend on the duplex alloy. Fabrication processes such as heat treating, welding, and hot working must consider the total time at temperature, as each cycle through the precipitation temperature range is cumulative, in order to avoid the loss of corrosion resistance and toughness.

The primary concern for the standard, super, and hyper duplex stainless steel grades is the formation of intermetallic compounds in the temperature range of 700 to 955 °C (1300 to 1750 °F). In this range these duplex stainless steels tend to form undesirable intermetallic compounds such as sigma phase or chi phase, *Figure 8*. Often this category of intermetallic compounds is called “sigma phase” because the different intermetallic phases are all detrimental to toughness and corrosion resistance, even if not precisely identified as sigma phase. These complex compounds of iron, chromium, and molybdenum are highly detrimental to corrosion resistance, particularly to the resistance to localised chloride attack, and toughness. The kinetics of sigma/chi precipitation is greatest in the range of about 815 to 925 °C (1500 to 1700 °F). The time required to produce detrimental effects on toughness and corrosion resistance typically depends on the temperature and the alloy content. The increased nitrogen content of second-generation duplex stainless steels significantly decreases the rate of the sigma/chi precipitation reactions making it possible to weld these grades without

Figure 8 Microstructure of a UNS S32205 plate aged at 900 °C (1650 °F) for 30 minutes showing large amount of sigma precipitation on the austenite/ferrite grain boundaries. NaOH etchant/Magnification 750X. (courtesy of Materials Technology Institute)

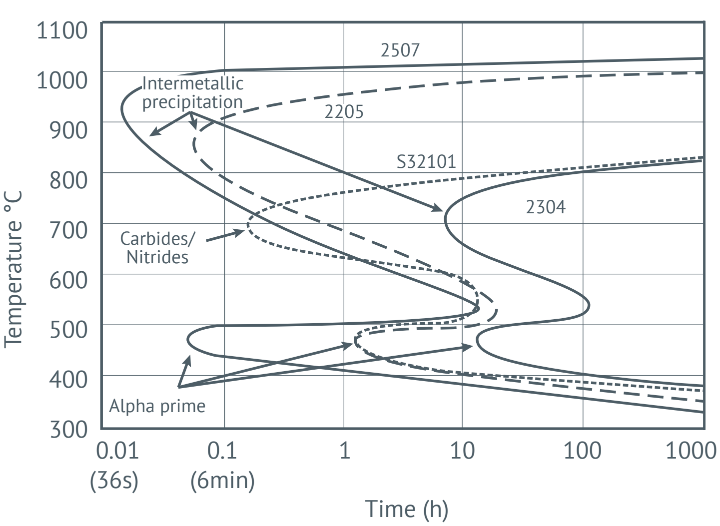


loss of properties. However, cooling rates after heat treatment and weld heat inputs and interpass temperatures must be controlled to avoid problems.

As shown in *Figure 9*, increased chromium and molybdenum contents will significantly shorten the times before there is a substantial loss of properties. For example, the super duplex grade Type 2507 (S32750) shows a loss in properties within a minute of exposure to temperatures in the 900 to 925 °C (1650 to 1700 °F) range, while Type 2304 (S32304) grade will only show a loss after about 80 minutes.

The duplex grades that are very lean in nickel and molybdenum such as S32101, will form intermetallic compounds but the required time in the sigma temperature range for their formation is very long, typically about 100 hours. Because of this, sigma formation is not a big concern with the lean duplex stainless steels. However, these lean duplex grades are susceptible to the loss of corrosion resistance and toughness due to carbide and nitride precipitation in the temperature range of 600 to 825 °C (1100 to 1500 °F). As shown in *Figure 9*, the time-at-temperature for a significant loss of properties with a lean grade such as S32101 is not much longer than that of the standard 2205 grade and similar control of temperature excursions must be practiced.

Figure 9 Isothermal precipitation diagram for various duplex stainless steels showing the temperature exposure required for a 50% reduction in impact toughness due to isothermal precipitation of undesirable phases (from reference 6)



Once formed, these compounds can only be removed by a full anneal with sufficient time to take the precipitates back into solution and homogenise to prevent their reoccurrence during cooling. Other than a full anneal above the stability temperature for the intermetallic phases followed by rapid cooling, no other remedy has been found to be effective.

If there is molybdenum segregation, as might remain from the initial solidification from the ingot or in particular the centre line of a concast slab, then it may be impossible to cool the steel rapidly enough through the critical temperature range to prevent the formation of intermetallic compounds. Centreline segregation can occur, but it tends not to be a practical problem as the segregated area is located in the middle of the plate and is not exposed to the service environment.

Alpha prime precipitation

Alpha prime is another undesirable phase that can form in the ferrite phase at temperatures between 315 and 525 °C (600 and 950 °F). The presence of alpha prime will result in a loss of ambient temperature toughness in the ferrite phase. The loss of properties occurs most readily at a temperature of approximately 475 °C (885 °F), *Figure 9* and is known as 475/885 embrittlement. Because of the need to avoid alpha prime precipitation many design codes limit the maximum temperature somewhere in the range 260-315 °C (500-600 °F), depending on the code.

Ductile-brittle transition

Duplex stainless steels have a wide range of applications but not quite the versatility of the austenitic grades. In the ideal duplex structure of nearly equal austenite and ferrite phases essentially free of intermetallic and nonmetallic compounds, the duplex grades show a gradual ductile-brittle transition. The duplex grades are suitable for use in arctic ambient conditions, as demonstrated by their success in many applications on the Alaskan North Slope, but not for cryogenic service.

Fabrication and welding

Cold forming

Forming operations on duplex stainless steels must take into account the fact that they are about twice as strong as the common austenitic grades and will work-harden rapidly.

However, because many designers take advantage of this higher strength for cost savings through thickness reduction, the increased resistance to forming may be offset by thinner sections.

Machining

The high strength and toughness tend to make most duplex grades more difficult to machine than the common austenitic stainless steels. Powerful, rigid machines with sharp tooling at lower speeds and heavy feeds will produce good machined parts in duplex stainless steels. One producer suggests that for carbide tooling, speeds should be reduced from those used for austenitic grades by 40% for roughing and about 20% for finishing.

Although most duplex stainless steel are significantly more difficult to machine than common austenitic grades, the lean S32101 grade is reported to have machinability that is superior to conventional austenitic stainless steels[8] and this excellent machinability is independent of the type of machining operation (milling, turning, drilling) or type of tools. The reasons for this superior machinability are not completely understood. A comparison of the machinability of selected austenitic and duplex stainless steels is given in *Tables 6 to 8*.

Welding

These steels are readily welded by all common arc welding processes. Ideally, the goal of welding a duplex stainless steel is for the weld metal and HAZ to have a joint with toughness and corrosion resistance equal to that of the base metal, however usually, the intent is for the weld metal and HAZ to be sufficiently high enough to suit the application or meet the fabrication specification requirements. The first step is to ensure that all the duplex is ordered and received with the proper chemistry (i.e. nitrogen in the higher end of the range) and in optimal heat treatment condition as shown by passing ASTM A923 or A1084 testing requirements. (See section Specifications and Quality Control.) If the material received has low nitrogen (but within the specification) or has small amounts of secondary phases present, it may not be possible to weld it and obtain satisfactory corrosion or toughness properties.

It is necessary to qualify each welding procedure to ensure heat input is neither too low nor too high. Low heat inputs can result in rapid cooling rates, which have the potential of producing a phase balance in the HAZ that is too high in ferrite. Too high of a heat input could expose the HAZ to the critical temperature range for the specific alloy for too long a time resulting in the precipitation of undesirable secondary phases. Because problems with duplex stainless steel welds reveal themselves by a loss of toughness or corrosion resistance, it is prudent that welding procedure qualifications include a toughness test (e.g. Charpy V-notch) at an appropriate temperature with acceptance criteria appropriate to the application, such as described in ISO 17781. Alternatively, because loss of corrosion resistance can be associated with precipitation of secondary phases, a corrosion test can also be used to evaluate weld procedures and it is not uncommon to have welds evaluated with both a toughness test and a corrosion test. Test methods for evaluating some common duplex stainless steel grades are:

Standard	Type of duplex
ASTM A923 / ISO 17781	Standard and superduplex
ASTM A1084 / ISO 17781	Lean

Higher nitrogen contents are extremely helpful in avoiding excessive ferrite content, especially with lower-alloyed grades. It is still necessary to be concerned about certain geometries, which can result in very rapid cooling rates, such as liner sheets installed on heavy plates or small welds on large plates. In extreme cases a modest preheat or a controlled interpass temperature for a multiple-pass weld will slow the cooling rate enough to allow sufficient reformation of austenite to produce good toughness and corrosion resistance.

The concern of too high heat input relates to the need to minimise the accumulated total exposure time of the HAZ in the critical temperature range. Even with a high nitrogen level, the total time at approximately 850 °C (1550 °F) before detrimental formation of intermetallic compounds is as short as five minutes for Type 2205 and only about one minute for the higher alloyed super duplex grades. This time must include both cooling after the final anneal and all subsequent fabrication. The ASTM A923, A1084 and ISO 17781 specifications were developed to provide test methods for detecting detrimental phases in duplex stainless steels. It is recommended that the appropriate A923, A1084 or ISO 17781 test methods be required to qualify duplex stainless steel weld procedures.

If intermetallics form in a HAZ of a large fabrication where post weld heat treatment is not a viable option, the only remedy may be to cut the weld and HAZ out and start over. Consequently, welding procedures must be qualified with respect to maximum thermal exposure, including any repair or rework practice. When later modifications of equipment are contemplated, it is important that total thermal history be considered before performing additional welding.

It is common for filler metals to contain increased nickel content to ensure that the rapidly quenched cast structure of the weld is comparable to the base metal in toughness and corrosion resistance. For example, the 2209 weld filler, most commonly used with Type 2205, has about 9% nickel, 3-4% more than the base metal. Matching welding fillers, over-alloyed with nickel, are available for many duplex grades and users are encouraged to contact the alloy producers for recommendations for specific grades. Only a few duplex filler metals are included in the welding standards such as AWS.

Weld metal toughness is strongly related to the welding process. Non-flux processes providing greater toughness. Typically, weld metal toughness as related to welding process is as follows:

GTAW> GMAW>FCAW>SMAW>SAW

Highly basic fluxes have been reported to be beneficial to the as-welded impact toughness of the duplex stainless steels.

When welding a duplex grade to carbon steel a Type 309L filler is usually a good choice for achieving a sound weld. An appropriate filler for joining 2205 or a super duplex grade to an austenitic stainless steel of lower molybdenum content would be 309LMo.

When installing a duplex stainless steel component in an existing austenitic stainless steel structure, consideration should be given to the relative strengths and expansion coefficients of the materials. The high strength of the duplex grade and their relatively low expansion coefficients may impose high stresses on the transition welds or the host structure.

Specifications and quality control

Most duplex stainless steels grades are covered in one or more of the many industry standards. *Tables 9* and *10* lists important ASTM standards and ASME coverage respectively, and some relevant international standards for duplex stainless steels are given in *Table 11*. Duplex stainless steels are included in the NACE MR0175/ISO 15156-3 international standard, which specifies environmental and material limits for the use of materials in service equipment used in oil and gas production. The duplex grades approved for use in the MR0175/ISO 15156-3 Standard include:

- S31803 (HIP);
- any duplex stainless steel with 30 ⩽ PRE number ⩽ 40, Mo ⩾ 1.5%;
- any duplex stainless steel with 40 < PRE number ⩽ 45; and
- where PRE number is $PRE = \%Cr + 3.3[\%Mo + 0.5(\%W)] + 16(\%N)$.

The S32101, S32304, S32003, S32202 and S32205 duplex stainless steels have approval in the NSF/ANSI Standard 61 for drinking water applications and may be used for pipes, tubes, storage tanks, and other products that come in contact with drinking water.

Many of the duplex stainless steels now have coverage in several API Standards:

- API 650 Welded Tanks for Oil Storage;
- API 5LC CRA Line Pipe; and
- API 938-C Use of Duplex Stainless Steels in the Oil Refining Industry.

It is essential that duplex stainless steel mill products be substantially free of intermetallic compounds and detrimental carbides and nitrides so that fabrication procedures can be designed to have the expected level of corrosion resistance and toughness. This issue is not addressed in the ASTM and ASME product specifications. It remains possible for a duplex stainless steel to meet all the requirements of the product specification and still be so affected by secondary phases that it is embrittled at low ambient temperatures or exhibits lower than expected corrosion resistance.

Although there are some safeguards in the qualification of fabricated structures, it is recommended that the end user and fabricator impose additional test requirements on duplex stainless steels to be certain that the base metal has the expected properties and the proposed welding procedures will not result in an unacceptable degradation of properties before investing in the large expense of fabrication.

For some of the more widely used duplex grades there are standard test methods for detecting the presence detrimental secondary phases in base metal and welds.

ASTM A923	Detecting Detrimental Intermetallic Phase in Duplex Austenitic/Ferritic Stainless Steels
ASTM A1084	Detecting Detrimental Phases in Lean Duplex Austenitic/Ferritic Stainless Steels
ISO 17781	Test methods for quality control of microstructure of ferritic/austenitic (duplex) stainless steels

These standards include three test methods:

- Metallographic examination to determine whether there is any visible evidence of undesirable secondary phases in the microstructure.
- A Charpy V-notch impact test to detect the precipitation of detrimental intermetallic phases. Although the impact testing is very effective at detecting a loss of properties due to the presence of undesirable phases, it is not easily and cheaply performed in all circumstances and may be sensitive to orientation and placement of the sample.
- A ferric chloride immersion corrosion test to detect the loss of corrosion properties associated with the presence of undesirable phases. (ASTM A1084 uses a ferric chloride/sodium nitrate solution.) The corrosion test methods can be performed on various shapes and product forms and they are regarded as very effective at detecting the presence of detrimental phases.

In the case of grades proprietary to a single producer, it is possible for the producer to use special quality controls and demonstrate to the user that the mill products meet a particular standard of quality. However, today there are many nonproprietary duplex stainless steel grades that are made by multiple producers. Because of this it is recommended that whenever possible product be required to pass the appropriate ASTM A923, A1084 or ISO 17781 impact test and/or ferric chloride test. In addition, it is also prudent to require water quenching of all products to reserve thermal exposure time for the fabricator, and testing is recommended for each plate or piece handled individually in heat treatment.

Applications

The large number of applications of duplex stainless steels across many industry sectors demonstrates the utility and versatility of these grades[9]. There are many second-generation cast duplex stainless steels now available, which have further increased the range of equipment fabricated from duplex stainless steels. The high strength, resistance to chloride SCC, other forms of SCC, increased availability, and relatively low cost compared to austenitic grades with similar corrosion resistance have resulted in increased use of duplex stainless steels across all industry sectors.

The lean duplex stainless steels with their relatively high strength and low cost make them ideal candidates for blast walls on offshore platforms, storage tanks for mildly corrosive liquids and structural applications, *Figure 10*. The SCC resistance of the duplex grades allows their use in heat transfer applications where Types 304L and 316L stainless steels have been unsatisfactory. For example, some breweries use the S32205 grade to overcome the problem of SCC of tanks and piping handling their hot potable water. Other applications include tubing for heat exchangers and embossed dimple jackets used to heat and cool vessels[10].

Figure 10 LDX 2101 (S32101) duplex stainless steel fermentation tank for the production of ethanol. (Courtesy of Outokumpu)

Transport applications include chemical tank trailers, which used the S32205 grades to overcome the thermal shock damage that can occur when loading hot corrosive chemicals into austenitic stainless steels tanks[11]. The high strength of duplex stainless steels also promises greater safety or increased payload through reduced material thickness. Ocean going tankers and chemical transport barges have been built in duplex stainless steels because of their strength and versatility in handling different chemical cargoes[12-14].

Due to their high strength and corrosion resistance in marine environments, duplex stainless steels have been used in many architectural applications, such as the Marina Bay Bridge in Singapore, *Figure 11*.

There has been extensive use of duplex stainless steels in oil and gas production equipment on land, in desert and arctic fields, offshore on fixed platforms and FPSO's and subsea because of its excellent combination of strength and resistance to the corrosive brines that occur naturally in the products. Down-hole piping, oil-gas separators, heat exchangers, process piping, pumps and valves have been constructed of various second-generation duplex stainless steels (see resource 1). Duplex stainless steel piping systems are also used in geothermal power applications.

Desalination plants are using more duplex stainless steels in thermal units for evaporator construction[15] and in reverse osmosis plants, *Figure 12*, for high pressure piping, seawater feed, brine reject piping, pumps, valves and energy recovery systems[16]. In the chemical process industries, there is growing use of duplex stainless steels for heat exchangers, pressure vessels, tanks, columns, pumps, valves, and shafting in a wide range of aggressive environments. The S32205 grade and lean duplex grades have been used to replace carbon-steel batch digesters[17] in the pulp and paper industry, *Figure 13*. In this application the high strength of the duplex stainless steel has allowed a reduction in wall thickness of about 38%.

Figure 12 Superduplex piping in a Seawater Reverse Osmosis desalination plant [Photo courtesy of Rolled Alloys]

Figure 11 Marina Bay Bridge in Singapore constructed entirely of 2205 duplex stainless steel [Courtesy of Outokumpu Stainless AB]

Figure 13 2205 batch digester for a Canadian pulp and paper mill

Additional Resources

There are various resources available to assist users and fabricators in the selection, fabrication, and use of duplex stainless steels. The following list provides some helpful resources:

1. R Francis, The Corrosion of Duplex Stainless Steels: A Practical Guide for Engineers, published by NACE International 2018.
2. *Welding Duplex and Super-Duplex Stainless Steels,* Nickel Institute Reprint Series No 14 036, 1993. (see website – nickelinstitute.org)
3. *Duplex Stainless Steels Microstructure, Properties and Application* Edited by Robert N Gunn, Woodhead Publishing Ltd, 1997.
4. J. V. Pellegrino, H. H. Stine, J. D. Fritz, and H. S. Ahluwalia, *Duplex Stainless Steel Atlas of Microstructures*, Materials Technology Institute, Inc., 2014.
5. *Practical Guidelines for the Fabrication of Duplex Stainless Steels*, International Molybdenum Association, 3rd edition, 2014. (see website – www.imoa.info)
6. *Welding Metallurgy and Weldability of Stainless Steels*, John C. Lippold and Damian J. Kotecki, A John Wiley & Sons, Inc. 2005.
7. *Welding of Duplex Stainless Steels,* TAPPI Technical Information Paper, TIP 0402-23, 2008. (see website - www.tappi.org)
8. O. Jonsson, M. Liljas, and P. Stenvall, *The Role of Nitrogen in Longitudinal Welding of Tubing in Duplex Stainless Steels*, acom 2-1994, Outokumpu Stainless AB, 1994.
9. Bjorn Holmberg, *How to Perform Welding in Duplex Stainless Steels To Obtain Optimum Weld Metal Properties*, acom 3-1997, Outokumpu Stainless AB, 1997.
10. Mats Liljas, *Choice of Specifications and Design Codes for Duplex Stainless Steels*, acom 4-2000, Outokumpu Stainless AB, 2000.
11. Jan Olsson, *Why Clad When There Is Duplex?*, acom 1-2005, Outokumpu Stainless AB, 2005.
12. Mats Benson, *Utilization of the Material Strength for Lower Weight and Cost with LDX 2101®* acom 3-2005, Outokumpu Stainless AB, 2005.
13. *Castings Stainless Steel and Nickel-Base*, Nickel Institute, Reference Book Series No 11 022.
14. Briony Holmes, *Guidelines for Measuring the Amount of Ferrite in Duplex Stainless Steels*, Materials Technology Institute, Inc., 2018.

References

1. J. V. Pellegrino, H. H. Stine, J. D. Fritz, and H. S. Ahluwalia, *Duplex Stainless Steel Atlas of Microstructures*, Materials Technology Institute, Inc., 2014.

2. D R McIntyre and R Francis (Eds), Environmental Cracking, published by MTI, 2016.

3. *High-Performance Stainless Steels,* No. 11 021, Nickel Institute, 2000

4. J. D. Fritz, B. W. Parks, J. F. Grubb, and C. P. Stinner, *The Use of Electrochemical Critical Pitting Temperature Measurements for Evaluating Stainless Steels*, Stainless Steel World 2001, Paper P10148, 2001.

5. *Practical Guidelines for The Fabrication of Duplex Stainless Steels*, International Molybdenum Association, 3rd edition, 2014.

6. Briony Holmes, *Guidelines for Measuring the Amount of Ferrite In Duplex Stainless Steels,* Materials Technology Institute, Inc., 2018.

7. Outokumpu product literature.

8. C. Bergquist and J. Olsson, LDX 2101®, a New Stainless Steel with Excellent Machining Properties, acom 4-2006, Outokumpu.

9. Jan Olson and Marie Louise Falkland *Versatility of Duplex*, Stainless Steel World Duplex America 2000 Conference Houston Paper - DA2-011.

10. B. J. Uhlenkamp and J. D. Fritz, *The Use of a Lean Duplex Stainless Steel, UNS S32101, for Thermal Dimple Jackets on Vessels for High Purity Applications,* NACE International, Corrosion 2007, Paper No. 07218, 2007.

11. Richard R, Staebler, *Comparison of Duplex to Austenitic Stainless Steels For DOT 407 and 412 Cargo Tanks In Liquid Chemical Service*, NACE International, Corrosion 1998 Conference & Expo, Paper No. 628, 1998.

12. Jacques Charles and Bruno Vincent, *Duplex Stainless Steels for Chemical Tankers*, 5th World Conference – Duplex Stainless Steels 97, Paper D97-018, 1997.

13. Thomas L. Ladwein, Volker Groß, Herbert Heuser, and Christian Koerber, *Use of 22% Chromium Duplex Stainless Steel for Chemical Cargo Vessels and Tank Trailers*, 5th World Conference – Duplex Stainless Steels 97, Paper D97-037, 1997

14. Bela Leffler, Hans Groth, and Arne Bergquist, *Advantages and Limitations of 2205 and Other Duplex Stainless Steels for the Transport of Chemicals*, 5th World Conference – Duplex Stainless Steels 97, Paper D97-018, 1997.

15. Jan Olsson and Viktor Jagerstrom, *MSF Chambers of Solid Duplex Stainless Steel*, IDA World Congress on Desalination and Water Reuse, Paradise Island, Bahamas, 2003.

16. Jan Olsson, and Kenan Cosic, *Stainless Steels for SWRO Plants High-Pressure Piping, Properties, and Experience*, IDA World Congress on Desalination and Water Reuse, Paradise Island, Bahamas, 2003.

17. Johan Nordstrom, *Digesters and Pulp Storage Towers of Duplex Stainless Steels – Saving Weight and Costs*, acom 3-1994, Outokumpu Stainless AB, 1994.

Nickel INSTITUTE

knowledge for a brighter future

Nickel Institute
communications@nickelinstitute.org
www.nickelinstitute.org

Published 2020