INTRODUCTION TO DUPLEX STAINLESS STEELS

INTRODUCTION

The application of duplex stainless steels has expanded rapidly over the last decade. Traditionally, the standard duplex grade, 2205 (S32205) has been used for chloride environments, requiring greater stress corrosion cracking than 300 series austenitic stainless steel grades. With the development of leaner grades and more alloyed super and hyper grades, the use of DSSs has expanded to very demanding applications such as seawater and various chemical processing environments and also to applications where only low corrosion resistance is required, such as building and architecture.

Duplex stainless steels are called "duplex" because they have a two-phase microstructure consisting of grains of body-centered cubic ferrite phase and face-centered cubic austenite phase. When duplex stainless steel is melted it solidifies from the liquid phase to a completely ferritic structure. As the material cools to room temperature, about half of the ferritic grains transform to austenitic grains ("islands"). The result is a microstructure of roughly 50% austenite and 50% ferrite. Figure 1 shows the typical microstructure of mill-annealed and water-quenched wrought super duplex stainless steel microstructure of grade S32520.

The duplex structure gives this family of stainless steels a combination of attractive properties:

Strength: Based on yield strength, duplex stainless steels are about twice as strong as regular austenitic or ferritic stainless steels.

Toughness and ductility: Duplex stainless steels have significantly better toughness and ductility than ferritic grades; however, they do not reach the excellent values of austenitic grades.

Corrosion resistance: As with all stainless steels, corrosion resistance depends mostly on the alloy composition. For chloride pitting and crevice corrosion resistance, their chromium, molybdenum and nitrogen content are most important. Duplex stainless steel grades have a range of corrosion resistance, similar to the range for austenitic stainless steels, i.e., from Type 304 or 316 (e.g., LDX 2101) to 6% molybdenum (e.g., 2507) stainless steels.

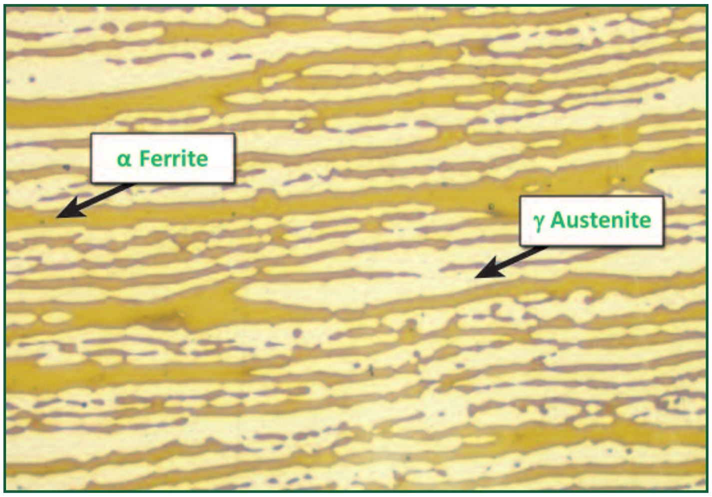

Figure 1 – Mill-annealed and water-quenched wrought DSS (S32520). Microstructure contains approximately equal amounts of austenite (light phase) and ferrite (dark phase). Magnification, 1000X.

An empirical relationship based on chemical composition, referred to as pitting resistance equivalent number, (PREN) is often used to predict the relative pitting performance of austenitic and duplex stainless steels. It is expressed as PREN = Cr + 3.3 (Mo + 0.5 W) + 16N.

Stress corrosion cracking resistance: Duplex stainless steels show very good stress corrosion cracking (SCC) resistance, a property they have "inherited" from the ferrite phase. Because SCC can be a problem under certain circumstances (chlorides, humidity, and elevated temperature) for standard austenitics such as Types 304 and 316, the duplex grades are often selected for enhanced SCC resistance.

Cost: Duplex stainless steels have lower nickel and molybdenum contents than their austenitic counterparts of similar corrosion resistance. Due to the lower alloying content, duplex stainless steels can be lower in cost, especially in times of high alloy surcharges. Additionally, it may often be possible to reduce the section thickness of duplex stainless steel, due to its increased yield strength compared to austenitic stainless steel. The combination can lead to significant cost and weight savings compared to the same construction in austenitic stainless steels.

CHEMICAL COMPOSITION

The duplex stainless steels are loosely divided into categories depending on the level of alloying or by their corrosion resistance. Table 1 lists some of the common grades of duplex stainless steels.

Lean DSSs are characterized by having relatively low levels of nickel (Ni) and/or (Mo). To compensate for the reduced (Ni), which is a strong austenite former, the (N) and manganese (Mn) levels are increased to provide an acceptable balance of austenite (γ) and ferrite (α). As a group, the ***lean*** DSSs have a very good combination of strength and corrosion resistance, and typically exhibit PREs of about 24. Most lean grades have PRENs equal to or just below that of 316L.

The ***standard*** DSS grades typically contain 22 to 25% [Cr] and 2 to 3% [Mo]. Grades in this category are used widely across all industry sectors. Type 2205 (UNS32205) DSS has evolved into the workhorse grade and is by far the most widely used of all DSSs.

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. If product specifications require the use of the S31803 designation, and if specifications permit, users can benefit by dual specifying S32205 along with Grade S31803. Products of S32205 have a composition that also meets requirements for the S31803 designation. Although not rigorously defined, the standard grades have a PREN range of about 30-39.

The ***super*** DSSs typically contain 25% [Cr], 3.5-4.0% [Mo], 0.5% Copper [Cu] and 0.25-0.27% [N] (and Tungsten [W] when used). These alloys have corrosion resistance equivalent to super austenitic stainless steels containing 6% molybdenum. These groups of DSSs have a PREN of 40-45.

Grade (UNS S32707) DSS is a highly alloyed super version designed for aggressive acidic and chloride-containing environments. Because this grade is more highly alloyed than the super duplex stainless steels, the term ***hyper*** DSS is sometimes used to describe this category of alloy and to distinguish it from the super duplex grades. This group of DSSs has a PREN of greater than 45.

MICROSTRUCTURE

The chemical composition of duplex steels is balanced to give approximately equal amounts of ferrite and austenite in solution annealed condition. The higher the annealing temperature the higher the ferrite content.

Duplex stainless steels are prone to precipitation of sigma phase (σ) and chi (χ) phase when exposed to temperatures in the range 700-955ºC. These undesirable intermetallic compounds can result in embrittlement and reduced corrosion resistance. The occurrence of these phases is usually associated with fabrication and processing practices such as excessively high weld heat inputs or slow cooling rates after solution anneal heat treatments.

TABLE 1 – Nominal Compositions (wt%) of Common Wrought Duplex Stainless Steels

UNS Designation	Type	EN	Cr	Mo	Ni	Cu	Mn[(A)]	C[(A)]	N[(A)]	Other	PRE[(B)]
"Lean" Duplex Stainless Steels											
S32101		1.4162	21.0	0.3	1.5	–	4.0-6.0	0.04	0.20-0.25	–	24
S32304	2304[D]	1.4362	23.0	0.3	4.0	–	2.5	0.03	0.05-0.20	–	26
"Standard" Duplex Stainless Steels											
S32003			21.5	1.8	3.3	–	2.0	0.03	0.14-0.20	–	30
S31803	2205[D]	1.4462	21.0	2.7	5.0	–	2.0	0.03	0.08-0.20	–	31
S32205	2205[D]	1.4462	22.0	3.0	5.0	–	2.0	0.03	0.14-0.20	–	35
S32550	255[D]	1.4507	25.0	3.0	6.0	2.0	1.5	0.04	0.10-0.25	–	37
"Super" Duplex Stainless Steel											
S32705	2507[D]	1.4410	25.0	4.0	7.0	–	1.2	0.03	0.24-0.32	–	42
S32520		1.4507	25.0	4.0	6.5	0.8	1.5	0.03	0.20-0.35	–	41
S32760		1.4501	25.0	3.5	7.0	0.7	1.0	0.03	0.20-0.30	0.7 W	41
"Hyper" Duplex Stainless Steel											
S32707			27.0	4.8	6.5	–	1.5	0.03	0.30-0.50	1.0 Co	49

(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

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As shown in Figure 2, the increased [Cr] and [Mo] contents found in the higher alloyed steels will significantly shorten the times before there is a substantial loss of properties. For example, the super duplex grade, 2507, (S32750) shows a 50% loss of impact strength within a minute of exposure to temperatures in the 1650 to 1700ºF (900 to 925ºC) range, while the 2304 (S32304) grade will only show a loss after about 80 minutes.

The high temperature nose for the 2507 (S32750), 2205 (S32205), and 2304 (32304) grades shown in the time-temperature diagram in Figure 2 is due to σ/χ precipitation. Duplex grades that are very lean in Ni and Mo, such as LDX 2101® (S32101) require very long times (8 to 10 hours) before intermetallic precipitation occurs. However, as shown in Figure 2, the LDX 2101® (S32101) grade does show a rapid loss of properties at temperatures in the 650 – 750ºC range, which is due to the precipitation of carbides and nitrides.

Alpha prime (α') is another undesirable phase that can form in the α-ferrite phase at temperatures between 600 and 950ºF (315 and 525ºC). The presence of (α') will result in a loss of ambient temperature toughness in the (α) phase. The loss of properties occurs most readily at a temperature of approximately 885ºF (475ºC) (see Figure 2) and is known as 885ºF/475ºC embrittlement. Because of the need to avoid (α') precipitation, most DSSs have a maximum service temperature of about 600ºF (316ºC).

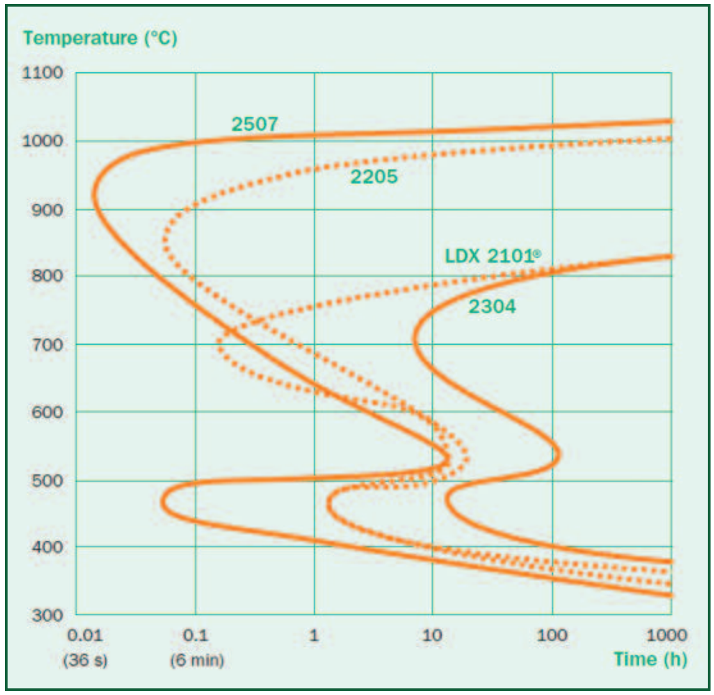

Figure 2 – Time - temperature exposures required for a 50% reduction in impact strength due Isothermal precipitation of undesirable secondary phases diagram for various duplex stainless steels. (Reference Outokumpu literature)

MECHANICAL PROPERTIES

Duplex stainless steels have exceptional mechanical properties. Their room temperature yield strength in the solution-annealed condition is more than double that of standard austenitic stainless steels not alloyed with nitrogen. This may allow the designer to decrease the wall thickness in some applications. The typical mechanical properties of hot rolled plate are shown in Table 2.

CORROSION RESISTANCE

Duplex stainless steels exhibit a high level of corrosion resistance in most environments where the standard austenitic grades are useful. However, there are some notable exceptions where they are decidedly superior. This results from their high chromium content, which is beneficial in oxidizing acids, along with sufficient molybdenum and nickel to provide resistance in mildly reducing acid environments. The relatively high chromium, molybdenum and nitrogen also give them very good resistance to chloride pitting and crevice corrosion. Their duplex structure is an advantage in potential chloride stress corrosion cracking environments. Duplex alloys are more resistant to chloride stress corrosion cracking than Types 304 and 316.

PITTING AND CREVICE CORROSION RESISTANCE

The high chromium, molybdenum and nitrogen contents in duplex grades provide very good resistance to chloride-induced localized corrosion in aqueous environments. All but the very lowest alloyed duplex stainless steels are far superior to Type 316 in this respect. Depending on the alloy content, some duplex grades are among the best performing stainless steels. Because they contain relatively high chromium content, duplex stainless steels provide a high level of corrosion resistance very economically. A comparison of pitting and crevice corrosion resistance for a number of stainless steels in the solution annealed condition as measured by the ASTM G 48 procedures (10% ferric

TABLE 2 – Typical Mechanical Properties of Hot Rolled Duplex Plate

UNS Designation	Type	EN	0.2% Yield Strength (KSI)	Tensile Strength (KSI)	Elongation %	Hardness (HB)
S32101	Lean	1.4162	72.5	101.5	38	225
S32304	Lean	1.4362	65.3	97.2	40	210
S32205	Standard	1.4462	73.9	108.7	35	230
S32705	Super	1.4410	84.1	120.4	35	250

chloride) is given in Figure 3. Critical temperatures for materials in the as-welded condition would be expected to be somewhat lower. Higher critical pitting (CPT) or crevice corrosion temperatures (CCT) indicate greater resistance to the initiation of these forms of corrosion. The CPT and CCT of 2205 are well above those of Type 316. This makes 2205 a versatile material in applications where chlorides are concentrated by evaporation, as in the vapor spaces of heat exchangers or beneath insulation. The CPT of 2205 indicates that it can handle many brackish waters and de-aerated brines. It has been successfully used in seawater applications where the surface has been maintained free of deposits through high flow rates or other means.

STRESS CORROSION CRACKING

Stainless steel can be affected by stress corrosion cracking (SCC) in chloride containing environment at elevated temperatures. Conventional austenitic stainless steel is particularly vulnerable to stress corrosion cracking while stainless steels of the duplex type are less susceptible to this type of corrosion.

Different methods are used to rank stainless steel grades with regard to their resistance to stress corrosion cracking and results may vary depending on the test method as well as test environment. In Table 3 a comparison is given of the stress corrosion cracking resistance of conventional austenitic stainless steels and duplex stainless steels for a number of accelerated laboratory tests. These methods include immersion tests in several chloride solutions as well as the Wick test (ASTM C 692) which is performed under evaporative conditions. *The test data was developed by Outokumpu Stainless Steel.*

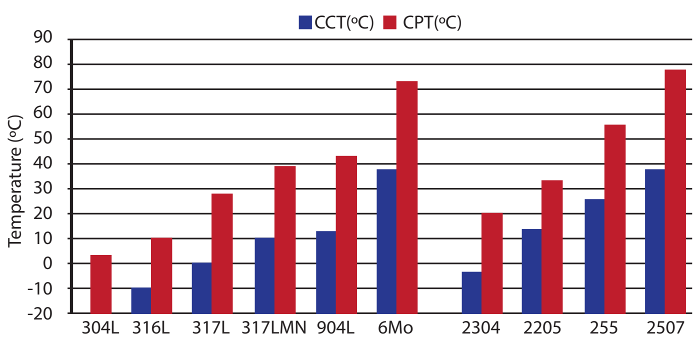

Figure 3 – Critical Pitting and Crevice Corrosion Temperatures for Unwelded Stainless Steels in the Solution Annealed Condition (Evaluated in 10% ferric chloride by ASTM G48)

The results show that while duplex stainless steels are not immune under very harsh conditions, such as boiling concentrated magnesium chloride, they withstand stress corrosion cracking under many conditions where conventional austenitic grades are expected to fail.

WELDING

The goals of welding DSS are to achieve a strength, toughness, and corrosion resistance in the weld metal and heat-affected zone equal to that of the base metal. To accomplish this, the welding operation must use an appropriate filler, achieve an acceptable austenite/ferrite balance in the weld and HAZ, and avoid undesirable secondary phases. To assist in evaluating weld microstructures, this atlas includes microstructures of various welded duplex grades both in the as-welded condition and the aged condition to produce undesirable phases.

It is prudent to qualify each welding procedure to ensure heat input is neither too low or too high. Low heat inputs can result in rapid cooling rates, which can produce an excessive amount of ferrite in the HAZ. The higher nitrogen contents in today's duplex stainless steels are very helpful in avoiding excessive ferrite content. However, it is still necessary to be concerned about certain geometries such as thinner sheets installed on heavy plates or small welds on large plates.

Excessive heat input could expose the HAZ to the critical temperature range of 815 to 925ºC (1500 to 1700ºF) for too long a time resulting in the precipitation of sigma/chi phases. Because of this, the heat inputs and high interpass temperatures for multiple pass welds, particularly on thick sections, must be controlled.

Problems with duplex stainless steel welds reveal themselves by a loss of toughness and it is prudent that welding procedure qualifications include a toughness test with acceptance criteria appropriate to the application.

Table 3 - Summary of Comparative Stress Corrosion Cracking Resistance in Accelerated Laboratory Tests

Test Solution Temperature Load	ASTM G 36 45% MgCl 155ºC (b.p.) U-bend	40% $CaCl_2$ (100ºC) U-bend	40% $CaCl_2$ (100ºC) 0.9x$R_{p0.2}$ (4-PB)	ASTM G 123 25% NaCl, pH 1.5 106ºC (b.p) U-bend	25% NaCl 106ºC (b.p.) U-bend	ASTM C 692 1500 ppm CL 100ºC $R_{p0.2}$
4307	Expected	Expected	Expected	Expected	Expected	Expected
4404	Expected	Expected	Possible	Expected	Possible	Expected
LDX 2101®	Expected	Not Anticipated	Not Anticipated	Not Anticipated	Not Anticipated	Not Anticipated
2304	Expected	Not Anticipated	Not Anticipated	Not Anticipated	Not Anticipated	Not Anticipated
LDX 2404®	Expected	Possible	Not Anticipated	Not Anticipated	Not Anticipated	Not Anticipated
2205	Expected	Not Anticipated	Not Anticipated	Not Anticipated	Not Anticipated	Possible
2507	Expected	Not Anticipated	Not Anticipated	Not Anticipated	Not Anticipated	Not Anticipated

b.p. = boiling point. Expected = SCC is expected to occur. Not Anticipated = SCC is not expected to occur. Possible = SCC may occur. Data obtained from Outokumpu literature

Additionally, because loss of corrosion resistance can be associated with precipitation of undesirable phases, the use of a corrosion test, such as that suggested in ASTM A923, to evaluate weld procedures is suggested.

It is common for weld 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, which is widely used for welding the 2205 grade, has about 9% nickel compared to the 5% that is typically found in the 2205 base metal. Because of this it is common to find more austenite phase in the weld than either the HAZ or base metal. Matching fillers are available for most duplex grades and users are encouraged to contact the alloy producers for recommendations for specific grades.

SPECIFICATION AND QUALITY CONTROL

Most DSS grades are covered in one or more of the many industry standards. Table 4 lists important ASTM standards.

It is essential that DSS mill products be substantially free of intermetallic compounds 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, however, it may be prudent to impose additional test requirements on DSS 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.

For some of the more widely used duplex grades there are ASTM standard test methods for detecting the presence of detrimental intermetallic phases in base metal and welds (see ASTM A923). In this standard the Test Method A consists of a metallographic examination to determine whether there are any visible secondary phases in the microstructure. This test method may be used for the acceptance of material but not for rejection.

Test Method B consists of a Charpy impact test at lower temperatures, typically -40°C (-40°F), to ensure minimum impact energy. Although the impact testing is very effective at detecting a loss of properties due to the presence of intermetallic phases, it cannot be used on all product forms and is a relatively expensive test.

Test Method C uses a ferric chloride immersion corrosion test to detect the loss of corrosion properties associated with the presence of undesirable intermetallic compounds. This test method can be performed on various shapes and product forms and it is effective at detecting sigma.

ASTM A1084 is a standard test method for detecting detrimental phases in lean duplex stainless steels. This standard includes a metallographic examination, a Charpy impact test, and an inhibited ferric chloride corrosion test that were all specifically developed for evaluating lean duplex stainless steel grades.

Table 4 – Summary of ASTM standards and the applicable UNS DSS grades

Relevant ASTM Specification	Covered UNS Duplex Stainless
A 182 – Forged or Rolled Alloy and Stainless Steel Pipe Flanges, Forged Fittings, and Valves and Parts for High Temperature Service.	S32205, S31200, S32950, S32550, S32750, S32520
A 240 – Chromium and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Pressure Vessels and for General Applications	S31200, S31260, S31803, S32001, S32003, S32101, S32205, S32304, S32506, S32520, S32550, S32750
A 270 – Seamless and Welded Austenitic and Ferritic/Austenitic Stainless Steel Sanitary Tubing	S31803, S32205, S32750, S32003
A 276 – Stainless Steel Bars and Shapes	S31100, S31803, S32101, S32205, S32304, S32506
A 479 – Stainless Steel Bar and Shapes for Use in Boilers and Other Pressure vessels	S31803, S32101, S32205, S32506, S32550, S32750
A789 – Seamless and Welded Ferritic/Austenitic Stainless Steel Tubing for General Service	S31803, S32205, S31500, S32550, S31200, S31260, S32001, S32304, S39274, S32750, S32760
A 790 – Seamless and Welded Ferritic/Austenitic Stainless Steel Pipe	S31803, S32205, S31500, S32550, S31200, S31260, S32304, S39274, S32750, S32760, S32900, S32950
A 815 – Wrought Ferritic, Ferritic/Austenitic, Martensitic Stainless Steel Piping Fittings	S31803, S32750, S32950, S32760, S39274, S32550
A 928 – Ferritic/Austenitic (Duplex) Stainless Steel Pipe Electric Fusion Welded with Addition of Filler Metal	S31200, S31260, S31500, S31803, S32205, S32304, S32550, S32750, S32900
A 923 – Detecting Detrimental Intermetallic Phase in Duplex (Austenitic/Ferritic) Stainless Steels	S31803, S32205, S32750

This guide was produced by Penn Stainless Products, Inc., in collaboration with "Dr. Metals", Hira Ahluwalia, Ph.D., scientist, metallurgist, materials and corrosion consultant to some of the world's largest industrial consortiums, and president of Material Selection Resources, Inc.

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Printed in U.S.A. PSP-169 10-14