Langley Alloys

An Introduction to Duplex and Super Duplex Stainless Steels

Duplex

Summary Duplex stainless steels

- provide high levels of yield strength and good levels of impact strength
- achieve excellent levels of corrosion resistance in a wide variety of mediums
- can be confidently specified for applications between -50˚C and +250˚C
- are resistant to stress corrosion cracking
- can be readily machined, fabricated and welded with the correct tooling and procedures
- offer unbeatable levels of cost competitiveness versus more expensive alloys

Introduction

Duplex stainless steels are so-called due to their combination of austenitic and ferritic microstructures, in an approximately 50:50 ratio. The microstructure of an alloy is another way to describe the crystal structure of the atoms, and it is important as it defines many of the alloy's properties. Whereas the most common 3xx and 4xx stainless steels are exclusively austenitic or ferritic in structure respectively, duplex stainless steels combine the most attractive features of both.

A family of duplex stainless steels

The Schaeffler diagram is a useful tool that indicates the microstructure of an alloy based upon its chemical composition. The presence of elements such as chromium, silicon, molybdenum, niobium and tungsten (chrome equivalent content) tend to favour the existence of a ferritic microstructure, whilst the presence of carbon, nickel, manganese, copper and nitrogen (nickel equivalent content) tend to favour the existence of an austenitic microstructure.

Adding together the content of the nickel - and chrome-equivalent elements allows the reader to predict the structure (and therefore the properties and characteristics) of a given alloy from the chart below.

i) Alloy costs

One obvious feature of the Schaeffler diagram is how close a number of the most common (3xx and 4xx) alloys are to the boundaries of a particular microstructure. As the different elements used can vary considerably in cost, an important aspect of alloy design is maintaining the favourable properties without compromising cost. Therefore 304/316 will use the minimum amount of expensive nickel in order to remain fully austenitic. Ferritic (4xx) and martensitic (17/4 PH) grades follow a similar pattern, albeit with different elements.

An important feature of duplex and super duplex stainless steels is their ability to achieve excellent levels of strength and corrosion resistance in addition to competitive costs. The widespread use of nitrogen as an alloying addition was one of the main drivers for their development. Not only does this element improve the overall corrosion resistance, but it also acts as a nickel-equivalent - substituting a high-cost element with a low-cost element.

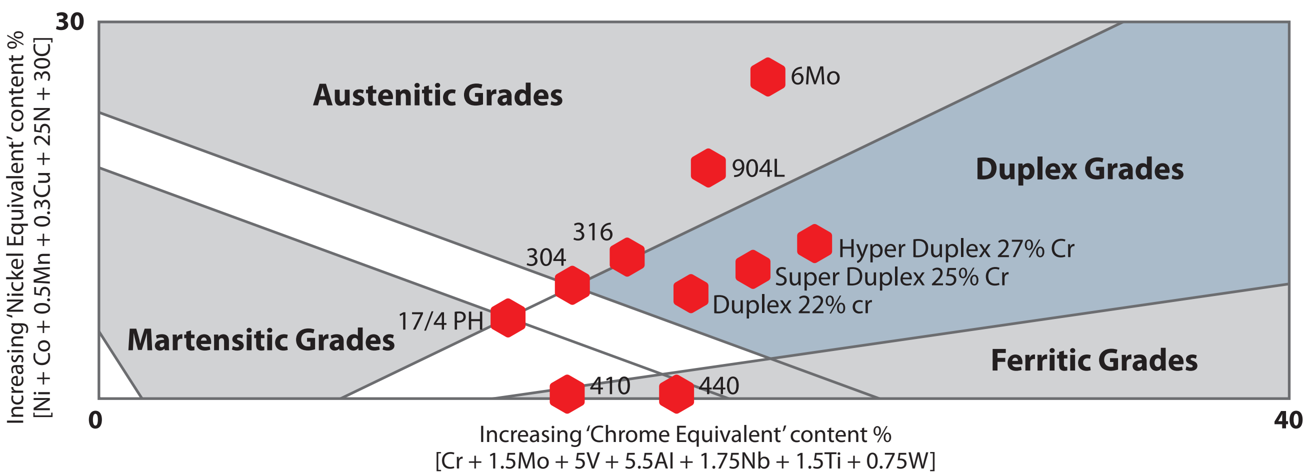

Figure 1. Schaeffler Diagram, highlighting the position of duplex alloys.

	Ferritic	Austenitic	Duplex	Martensitic
Corrosion resistance	★★★	★★★ Standard ★★★★★ Super	★★★★★	★★ ★★★
Stress Corrosion Cracking	★★★★★	★★	★★★★	★★★★
Strength	★★★	★★	★★★★★	★★★★★
Tough (low temps)	★★	★★★★★	★★★	★★
Formality	★★	★★★★	★★★	★★
Weldability	★	★★★★★	★★★★	★
Non-magnetic	★	★★★★★	★★★	★

Figure 2. An overview of stainless steel properties depending upon microstructure (1=low, 5=high)

ii) Alloy types

At a very simplistic level the high-level properties of each microstructure are summarised in the table. The table above is perhaps the clearest way to see how duplex stainless steels capture the most favourable aspects of both austenitic and ferritic microstructures.

iii) Corrosion resistance

Pitting Resistance Equivalent number (PREN) is a helpful theoretical way of comparing the pitting corrosion resistance of various types of metals based on their chemical compositions. The most widely accepted version of the PREN formula utilises the content of chromium, molybdenum and nitrogen as: PREN = %Cr + 3.3x %Mo + 16x %N.

The progression from duplex to super duplex to hyper duplex stainless steels can be clearly seen on the Schaeffler diagram. Increasing an alloy's content of chromium, molybdenum and nitrogen will increase its resistance to pitting corrosion. Duplex alloys typically have a PREN of >34, super duplex alloys are >40 and hyper duplex grades approach 50. Whilst it is not an exact science, and will depend upon the exact operating environment and product form, it is a helpful tool. The changes in composition also improve the strength of these alloys too.

Duplex Stainless Steels

Duplex stainless steels were originally developed in the 1930's for application in paper and pulp manufacture, based around a 22% Cr composition. Compared with the more common 3xx grades they replaced, these early duplex stainless steels offered twice the strength and a significant uplift in corrosion resistance.

Rather confusingly, there are two different designations for the most common type of duplex stainless steel. When originally developed, the grade was identified as UNS S31803 (F51). However, in order to enhance the resistance to pitting corrosion, steel manufacturers started to produce this grade with the composition of the key alloy additions at or near the maximum levels. In order to differentiate this enhanced product from the standard product it was re-designated as UNS S32205 (F60). As such S32205 meets the requirements of S31803 but not vice-versa.

Sandvik's Sanmac 2205 offers 'enhanced machinability as standard' compared with standard duplex grades, through careful control of the composition and production processes. The distribution of inclusions encourages chip-breaking, resulting in improved tool life and productivity gains.

Super Duplex Stainless Steels

Whilst concepts like the Schaeffler diagram and PREN equation suggest it is relatively easy to develop new and improved alloys, the complexities of production should not be understated. The desire to create higher performance alloys partly-coincided with the development of off-shore oil and gas exploration. Combining high strength to limit the weight of suspended components, with excellent corrosion resistance to operate in the UK's North Sea, were important objectives.

Ferralium (UNS S32550, 1.4507, F61) is the original super duplex stainless steel, patented by Langley Alloys in 1967 and launched in 1969. As such it was the very first alloy to be captioned as 'super duplex' and based around a 25% chromium content. Compared with later alternatives, it is the only grade to exceed a minimum yield strength of 85ksi, with an increased copper content for superior pitting corrosion resistance.

Alloy 32760 (UNS S32760, Zeron 100, 1.4501, F55) was developed in the 1980's by Mather & Platt (UK) around the same 25% chromium basis. However, it contains less copper but a deliberate addition of tungsten instead, claimed to selectively improve corrosion resistance.

The final grade most commonly stocked as solid bar is **Alloy 32750** (UNS S32750, 1.4410, F53) which is promoted by Sandvik as SAF2507 (Alloy 2507). It contains neither copper nor tungsten as significant additions.

Composition of Duplex and Super Duplex Stainless Steels

As duplex and super duplex alloys have gained acceptance in the marketplace, the number of specifications has tended to proliferate. So-called lean duplex grades aim to match the performance of duplex grades, but reducing the content of expensive elements such as nickel. At the other extreme, hyper duplex stainless steels have been developed by Sandvik to rival the corrosion resistance of much more expensive nickel alloys. In all cases, mill- and customer-specific grades have been created, some more widely adopted in a particular product form i.e. as sheet or tubes only.

Both lean duplex and hyper duplex stainless steels are not commonly available in bar form.

The most common duplex stainless steel offered in bar form is S32205, which can be dual-certified as S31803. This accounts for around 2-3% of the global market for stainless steel bars.

The most common super duplex stainless steels in bar form are S32750, S32760 and Ferralium 255. These account for up to 2% of the global market for stainless steel bars.

The most noticeable differences in the composition of these three alloys is in the level of deliberate additions of copper and tungsten. Copper is widely recognised as improving the corrosion resistance to acids such as sulphuric acid, phosphoric acid and nitric acid. Ferralium 255 typically contains 2.0% copper, and as a consequence is highly specified in a number of chemical process industries, such as fertiliser and urea manufacture that use these acids within their process.

In addition, Ferralium 255 is specified with much lower levels of phosphorus and sulphur. This reduces the incidence and size of any inclusions, which if present at the surface of a component would be a potential source for pitting corrosion. It therefore contributes to the improved corrosion resistance of Ferralium 255 in practice.

> “Compared with the more common 3xx grades they replaced, these early duplex stainless steels offered twice the strength and a significant uplift in corrosion resistance.

	UNS Grade	Tradename	Cr	Ni	Mo	N	C	Mn	P	S	Si	Cu	Other
Lean Duplex	S32001		22.0 - 23.0	1.0 - 3.0	0.6	0.05 - 0.17	0.03	4.0 - 6.0	0.04	0.03	1	1	
	S32304	2304	21.5 - 24.5	3.0 - 5.5	0.05 - 0.60	0.05 - 0.20	0.03	2.5	0.04	0.03	1	0.05 - 0.60	
Duplex	S31200		24.0 - 26.0	5.5 - 6.5	1.2 - 2.0	0.14 - 0.20	0.03	2	0.045	0.03	1		
	S31260		24.0 - 26.0	5.5 - 7.5	2.5 - 3.5	0.1 - 0.20	0.03	1	0.03	0.03	0.75	0.2 - 0.8	W 0.1 - 0.2
	S31803		21.0 - 23.0	4.5 - 6.5	2.5 - 3.5	0.08 - 0.20	0.03	2	0.03	0.02	1		
	S32205	2205	22.0 - 23.0	4.5 - 6.5	3.0 - 3.5	0.14 - 0.20	0.03	2	0.03	0.02	1		
Super Duplex	S32520	255	24.0 - 26.0	5.5 - 8.0	3.0 - 4.0	0.20 - 0.35	0.03	1.5	0.035	0.02	0.8	0.5 - 2.0	
	S32550	255	24.0 - 27.0	4.5 - 6.5	2.9 - 3.9	0.10 - 0.25	0.04	1.5	0.04	0.03	1	1.5 - 2.5	
		Ferralium 255	24.5 - 26.5	5.5 - 6.5	3.1 - 3.8	0.20 - 0.25	0.025	0.80 - 1.20	0.025	0.005	0.7	1.5 - 2.0	
	S32750	SAF 2507	24.0 - 26.0	6.0 - 8.0	3.0 - 5.0	0.24 - 0.32	0.03	1.2	0.035	0.02	0.8	0.5	
	S32760	Zeron 100	24.0 - 26.0	6.0 - 8.0	3.0 - 4.0	0.20 - 0.30	0.03	1	0.03	0.01	1	0.5 - 1.0	W 0.5 - 1.0
	S32900	329	0.75	23.0 - 28.0	2.5 - 5.0	1.0 - 2.0		0.06	1	0.04	0.03		
Hyper Duplex	S32707	SAF 2707	27	6.5	4.8	0.4	0.03	1.5	0.035	0.01	0.5		Co 1.0
	S33207	SAF3207	32	7	3.5	0.5	0.03	1.5	0.035	0.01	0.8		

	UNS Grade	Tradename	Yield Strength (ksi)	Ultimate tensile Strength (ksi)	Elongation (%)
Lean Duplex	S32001		65	90	25
	S32304	2304	65	90	25
Duplex	S31200		65	100	25
	S31260		65	100	25
	S31803		65	90	25
	S32205	2205	65	90	25
Super Duplex	S32520	255	80	109	25
	S32550	255	80	109	25
		Ferralium 255	85	115	25
	S32750	SAF 2507	80	109	15
	S32760	Zeron 100	80	109	25
	S32900	329	65	90	20
Hyper Duplex	S32707	SAF 2707	101	116	25
	S33207	SAF3207	101	123	25

Figure 3. Sanmac 2205 offers 'enhanced machinability as standard' with improved chip-breaking properties.

Mechanical Properties of Duplex and Super Duplex Stainless Steels

The yield and tensile strength of this family of alloys will generally increase as you progress from duplex to super duplex to hyper duplex variants. Duplex stainless steels are the logical next-step when looking for improved performance over standard 304/316 austenitic alloys, whilst super duplex stainless steels are close enough to the most popular nickel alloys to make them worthy of consideration.

Through careful control of the composition and processing conditions, Ferralium 255 is able to achieve a higher yield strength compared with S32750 and S32760 (85ksi vs. 80ksi). This increase can be beneficial in components where weight is an issue, such as in suspended loads. It can also be used to reduce the size of critical components.

Stress corrosion cracking occurs when metal components are exposed to a combination of tensile stresses and a corrosive environment. It is particularly relevant to alloys used in oil and gas applications, as the presence of hydrogen sulphide (H2S) in 'sour' fields can greatly exacerbate the corrosivity of natural seawater due to its acidic nature. Stress corrosion cracking can be avoided by using austenitic alloys of high corrosion resistance, but these will tend to be highly-alloyed, and therefore highly expensive. Alternatively, the mix of austenitic and ferritic grains within a duplex alloy slows and prevents the propagation of cracks within duplex and super duplex stainless steels. The most popular duplex and super duplex stainless steels are listed in NACE MR 0175 / ISO 15156 as being suitable for sour service.

Duplex and super duplex stainless steels can be widely used in operating temperatures from -50ºC to +250ºC. At the lower temperature, impact strength will fall away sharply, as it undergoes a ductile-brittle fracture transition. At the higher temperature, continuous service above this range will result in the precipitation of deleterious phases that impact mechanical properties and corrosion resistance.

Machining and Welding

Duplex and super duplex stainless steels require more care when machining than standard stainless steels. They are obviously higher strength, which puts greater stress on tooling and machinery. In addition, the chip formed is strong and abrasive to tooling. The absence of sulphur or other free-machining additives means that chip breaking is also more difficult too. Therefore, it is recommended to use tooling with carbide inserts and a positive chip-breaking geometry.

The phenomenon of 'movement' is also anecdotally reported for these grades. The presence of residual stresses within the original bar can lead to distortion, which is thought to be influenced by the mixed 'duplex' microstructure. Setting aside partly-machined components for any residual stresses to 'relax' between passes can help to minimise the extent of any movement. Stress relieving heat treatments can also be used for more challenging components such as long pump shafts. However, it should be noted that this operation may reduce the impact strength and corrosion resistance.

Welding has historically been a limitation for duplex and super duplex stainless steels, but should not be a concern as long as effective weld procedures are adopted. These grades are prone to the formation of harmful phases when exposed to elevated temperatures for a period of time. In poorly welded components, corrosion has been observed in the heat affected zone (HAZ) exposed to such undesirable conditions. The answer is to avoid excessive temperatures by controlling weld speed, plus limiting the inter-pass temperature in multi-run welds.

Applications for Duplex and Super Duplex Stainless Steels

Since their development in the 1930's, duplex stainless steels have been widely used in a variety of industrial processes where 304/316 grades are not sufficiently robust. Aside from paper and pulp manufacture, other common applications can be found in water treatment, architecture and marine hardware.

Given the additional performance of super duplex stainless steels, they are used in many demanding applications, including:

a) **Oil & Gas** – downhole tooling, wellhead and subsea equipment, pumps and valves all make use of super duplex alloys. As a family, these alloys are included in NACE MR1075 / EN15156-3 as being suitable for use in H2S-containing environments i.e. sour service wells.

b) **bolts and fasteners** – are a very common application of super duplex stainless steels, due to their very high starting strength and the possibility to work harden them to even higher strength levels.

c) **pollution control scrubbers** – this has been a successful application for super duplex stainless steels in the fabrication of precipitators, fans and pumps. These grades strongly resist corrosion in such environments; seawater is frequently used as a coolant, and acids such as sulphuric acid are formed from the emissions of the burnt fuel.

   The recent application of marine scrubbers are unable to exploit the excellent properties of these alloys, and are having to use more expensive super austenitic stainless steels instead. Legislation is forcing such vessels to selectively employ their scrubber systems in certain locations. When not in use, the scrubber will see temperatures beyond the sensible working range for duplex and super duplex alloys.

d) **marine applications** – propellers, shafts, rudders and seals are frequently supplied in super duplex grades, when austenitic stainless steels such as XM-19 are not deemed acceptable on the grounds of either corrosion resistance or strength.

e) **chemical process industry** – a large number of processes will utilise sulphuric acid, nitric acid and phosphoric acid, such as in the production of PP, PVC, TiOx, dyes and agrochemicals. Fortunately, super duplex stainless steels are generally resistant to reducing acids, as well as offering good abrasion and wear resistance.

   Ferralium 255 is widely specified in the production of fertilisers, as mixers, tanks and vessels, pumps and valves, as it strongly resists corrosion from the acids used (sulphuric, phosphoric or nitric acid) and the mechanical impact of 'phos rock'.

f) **vegetable processing** – a less obvious application has been in the construction of equipment for processing grains and vegetables, The severe wear and corrosion ('erosion corrosion') conditions involved in sugar cane processing, mixers and centrifuges, have been well-served in Ferralium 255.

g) **water treatment** – associated applications such as sewage treatment, desalination and swimming pools all use super duplex grades to resist the threat of corrosion from seawater, contaminated or brackish solutions.

h) **paper and pulp** – most components throughout the production processes of pulp and paper can make use of super duplex alloys. Duplex and lean duplex grades are typically specified where possible on grounds of cost, but super duplex grades will be used in areas of greatest risk of failure.

i) **pump shafts** – this is a 'sweet spot' for super duplex stainless steels, exploiting the combination of high strength, wear and corrosion resistance.

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