

## **WELDS IN THE DUPLEX STAINLESS STEEL**

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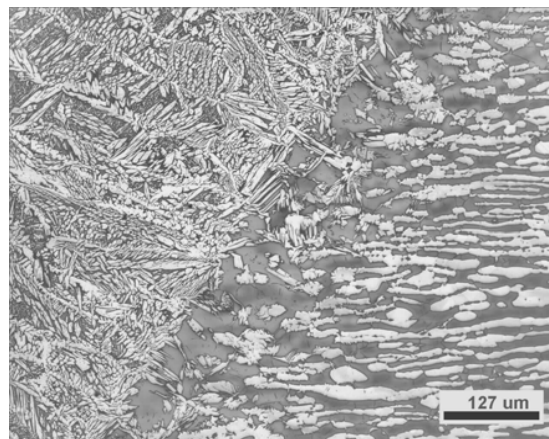
**Abstract:** Duplex stainless steels are a very attractive alternative to austenitic grades due to their higher strength and good corrosion performance. The austenitic grades can often be welded autogenously, while the duplex grades normally require addition of filler metal. This is to counteract segregation of important alloying elements and to give sufficient austenite formation to prevent precipitation of chromium nitrides that could have a negative effect on impact toughness and pitting resistance.

### **1. Duplex stainless steel**

The ferritic-austenitic grades have a ferrite matrix intermixed with austenite and are more commonly called ‘duplex’ stainless steels from the Latin ‘made up of two parts’. The duplex microstructure combines properties of both phases; the ferrite provides high strength and resistance to stress corrosion cracking (SCC), while the austenite contributes good ductility and general corrosion resistance.

Duplex stainless steels can be cost-effective alternatives to austenitic grades with equivalent corrosion resistance; especially in applications where the higher yield strength can be utilized in the design to decrease the wall thickness. Excellent resistance to localized corrosion in neutral and acidic chloride-containing solutions can be obtained owing to increased chromium, molybdenum and nitrogen contents.

Disadvantages of duplex grades are the moderate toughness and ferritization of the heat-affected zone (HAZ) after welding, which can reduce particularly pitting corrosion resistance. In addition, proneness to embrittlement after thermal aging, limits the maximum service temperature to 260–300°C. A typical duplex weld microstructure is shown in Figure 1.



**Fig.1. Typical duplex weld microstructure**

There are numerous commercial duplex stainless steels available. These normally contain 20–29% Cr, 1–8% Ni, 0–4.5% Mo, 0.1–0.3% N and 0.02–0.03% C. It is popular to differentiate the different grades by the alloying content affecting the corrosion properties, and the pitting resistance equivalent;  $PRE = \%Cr + 3.3 \times \%Mo + 16 \times \%N$  [10,11], is generally accepted as a rough estimation of the corrosion resistance of duplex grades.

The factor given for nitrogen in the literature varies between 10 and 30, but 16 is the most frequently cited value for duplex grades.

The resistance to pitting corrosion in neutral chloride-containing solutions increases with higher PRE numbers, but this should only be considered as an indication. Also other elements such as manganese, tungsten, sulphur and carbon may affect the pitting performance.

#### 1.1 Lean duplex stainless steel

The recent fluctuations of primarily nickel price have promoted the alloy development towards leaner alloys to give a more stable alloying element cost. As a consequence, the expensive nickel has partly been substituted with nitrogen and manganese. The lean duplex grades have typically 20–24% Cr, 1–5% Ni, 0.1–0.3% Mo and 0.10–0.22% N.

These steels have a lean alloy content, resulting in lower cost and are, unlike most other duplex grades, only alloyed with small amounts of molybdenum. The lean alloy 2304 was developed to compete primarily with the austenitic AISI 316 grade, but with twice the yield strength and significantly better resistance to SCC.

The PRE is about 24–25, which is about the same as that of the 316L steel, giving equal or often even higher pitting resistance. The low molybdenum content also leads to similar resistance to AISI 304L in nitric acid. The weldability of this type of duplex steel is generally good when using slightly over-alloyed filler metal. The newly developed lean duplex grade LDX 2101R with 1.5% nickel has 0.22% nitrogen and 5% manganese.

It is shown in this work that LDX 2101 has such improved weldability that also autogenous welding is possible [B,C] and this material has contributed to the boom in the lean duplex market.

#### 1.2 Standard duplex stainless steel

The dominant commercial duplex stainless steel type contains 21–23% Cr, 4.5–6% Ni, 2.5–3.5% Mo and 0.10–0.22% N and is designated 2205. This steel was developed in the 1970s, but was later optimised with higher nitrogen levels for improved weldability. The PRE of 2205 is about 33–35 resulting in a resistance to localized corrosion intermediate between the austenitic grade AISI 317 and the 5–6% Mo super austenitic alloys.

The weldability of this grade is good, but overmatching filler with increased nickel content, e.g., is normally required for optimum weld metal properties.

#### 1.3 Superduplex stainless steel

The superduplex stainless steels typically contain 24–29% Cr, 4.5–8% Ni, 2.7–4.5% Mo, 0.1–0.35% N and are in some cases alloyed with copper and tungsten. These grades are characterised by a PRE > 40.

The superduplex grades were developed to withstand very aggressive environments to compete with super-austenitics and nickel base alloys. 2507 has, due to high molybdenum and nitrogen contents, a PRE of 42–43, and offers high mechanical strength and corrosion resistance in extremely aggressive environments such as chloride-containing acids.

A consequence of the high alloy content, there is a risk of precipitation of intermetallic phases, limiting the heat input and interpass temperatures when multipass welding.

Overmatching filler with increased nickel content is required, e.g. 2509, to compensate element partitioning for optimum corrosion resistance.

#### 1.4 Hyperduplex stainless steel

The new hyperduplex grade SAF 2707 HDR has a typical composition of 27% Cr, 6.5% Ni, 5% Mo and 0.4% N, with a PRE of 49. It was developed as a complement to 2507 with increased strength for use in even more aggressive conditions, such as in hot seawater,

acidic chloride solutions and organic acids [19]. SAF 2707 HD can be welded with a matching filler wire of ISO 27 9 5 L type. Due to the high alloying content, the hyperduplex alloys are somewhat more sensitive to secondary phase precipitation than the superduplex grades.

## **2. Welding of duplex stainless steel**

All fusion welding methods can be used for welding duplex stainless steels on condition that suitable welding procedures and consumables are used. Improper welding conditions can, however, have a negative effect on the corrosion resistance, toughness and ductility. Weld metal properties such as strength, toughness, corrosion resistance and SCC resistance can be impaired by a large deviation of the phase balance compared to the 3 parent metal. The weld microstructure is not only dependent on the chemical composition, but also on the welding parameters, which affect the thermal weld cycle.

Too high austenite fractions, which give a mixed ferrite-austenite solidification mode, can result in increased segregation and too high ferrite fractions can cause nitride precipitation, which can have a negative effect on the pitting resistance.

Consequently, the chemical composition of the weld metal is crucial and the solution normally is to add a filler wire specially developed for the particular grade. Welding consumables generally have a more austenitic composition with 2–4% more nickel than the parent steel for improved mechanical and corrosion properties. As nickel normally is considered to have a negligible influence on the pitting resistance in stainless steels the observed positive effect has been related to the role of nickel in controlling the weld microstructure.

Nickel also enhances the toughness of the weld metal. If no filler is added and no post weld heat treatment (PWHT) is applied after welding, nitrogen additions to the shielding gas can be an alternative. Nitrogen is an important alloying element in duplex grades and potential nitrogen loss from the weld metal during autogenous gas tungsten arc (GTA) welding can affect the corrosion resistance.

The driving force for such escape of nitrogen increases when welding nitrogen-alloyed grades, leading to a larger risk of losing the desired properties. This degassing process of nitrogen can cause a drop in PRE, also a more ferritic weld metal surface with chromium nitride precipitates in the ferrite grains exposed to the corrosive medium, hence impairing the resistance to pitting corrosion and the toughness. Nitrogen additions to the shielding and purging gas have been reported to be beneficial for the pitting resistance by preventing nitrogen loss.

## **3. Microstructure of duplex welds**

### **3.1. Solidification**

Most duplex stainless steels solidify in fully ferritic mode to  $\delta$  ferrite and no austenite is formed during the solidification, but in solid phase during the subsequent cooling. The ferritic solidification occurs as epitaxial growth of the ferrite grains from the fusion boundary and the dendrite growth is oriented in relation to the thermal gradient.

The resulting rather coarse columnar ferritic structure influences the final duplex structure as it provides the starting conditions for the further solid state transformations upon cooling.

Ferrite grain size and orientation can influence the weld cracking susceptibility as well as morphology and ferrite content of the final microstructure.

It has long been known that when the solidification occurs ferritically the partitioning of the metallic elements in the phases is not as strong as in the base metal. On the other hand, nitrogen is partitioned and enriched in austenite in solid state to a greater extent than in

the base metal. The chemical composition significantly affects the element distribution in the dendrites during solidification.

Chromium is often evenly distributed in the dendritic structure, while molybdenum, nickel and manganese mostly are segregated in between the dendrite cores. Segregation of important alloying elements and particularly of molybdenum is known to decrease the pitting resistance of high-alloyed weld metals.

Accordingly, most recommended welding consumables are designed to result in slightly over-alloyed weld metals. The retained segregation pattern does not, however, affect the austenite formation; since this is primarily controlled by the rapid diffusion of nitrogen and the dendritic substructure is often concealed by the nucleation and growth of austenite.

### 3.2. Austenite formation

As the solidification of duplex stainless steel weld metals is fully ferritic, diffusion controlled solid-state transformation to austenite occurs below the solidus temperature during subsequent cooling. This temperature range is determined by the chemical composition of the steel and naturally a more ferritic composition gives a wider ferrite range. The austenite formation has been suggested to be controlled by a paraequilibrium transformation mechanism in which the diffusion of nitrogen is the controlling process rather than diffusion of the slower moving metallic elements. A higher nitrogen alloying content will raise the ferrite-to-austenite transformation temperature and enhance the austenite growth rate.

Higher nitrogen levels both increase the driving force for austenite formation and decrease the temperature range where ferrite grain growth occurs. As the austenite transformation is a diffusion process, it is dependent on the cooling time. As high ferrite levels as almost 100% have been reported, in for instance, laser welds. At slower cooling rates, the transformation from ferrite to austenite occurs at significantly higher temperature producing more austenite and the width of the austenite at ferrite grain boundaries becomes wider.

### 3.3 Weld metal austenite morphology

During cooling, initially allotriomorphic austenite is rapidly precipitated along the ferrite grain boundaries in continuous networks and on further cooling, austenite precipitates as Widmanstätten side-plates growing into the grains. With sufficient time, austenite particles with acicular morphology may appear inside the ferrite grains. The rate of transformation is governed by a large number of factors, which are both process and material dependent.

These include the composition of the alloy and filler metal, and the dilution from the base metal. The welding parameters, in turn, influence the maximum temperature, time above the transformation temperature range and the cooling rate, which further affect the ferrite grain size, number of nucleation sites, nucleation rate, austenite growth and composition of the precipitated phases.

Also the level of inclusions can influence the austenite formation since inclusions are potential nucleation sites for intragranular austenite in the same way as the inclusions that promote acicular ferrite in low-alloy steel weld metals. Additional austenite formation can take place by subsequent reheating at elevated temperatures either when multi-pass welding or during PWHT.

### 3.4. Specification of phase balance

It is often specified that the weld metal ferrite content should be in the range of 35–65%, since excessively high ferrite contents are known to decrease the toughness and pitting resistance, and too low ferrite contents could decrease the resistance to SCC. However,

both experimental and practical experience has proven that rather good properties are obtained over a relatively large range of ferrite and austenite contents.

Over the range 30– 70% austenite, the phase balance has been shown to have minor importance. It thus seems more relevant to qualify a welding procedure by demonstrating with mechanical and corrosion testing that the procedure, when applied to the base material at the proposed thickness, will not deteriorate the toughness or corrosion resistance.

The relation between microstructure and properties is very complex and not fully understood. If the obtained microstructure deviated from the wanted one it does not necessarily mean that the properties are deteriorated but rather that a more thorough control of the material properties is needed. In fact, a round robin test performed by the International Institute of Welding (IIW) on identical duplex 2205 weld specimens showed that the scatter between different laboratories was as much as  $\pm 20\%$  of the measured mean value.

### 3.5. Secondary phases

Several unwanted secondary phases may form in duplex stainless steels and weld metals subject to temperatures in the range of 300–1100°C by heat treatment or welding operations. Exposure in this temperature range results in a more rapid precipitation in the weld metal than in the base metal due to the higher alloy content of the ferrite. The material producers often specify a maximum heat input to avoid excessively slow cooling rates. It should further be noted that repeated thermal cycles in multipass welds might have an additive effect in promoting precipitation and reduction in corrosion resistance.

#### 3.5.1. Chromium nitrides

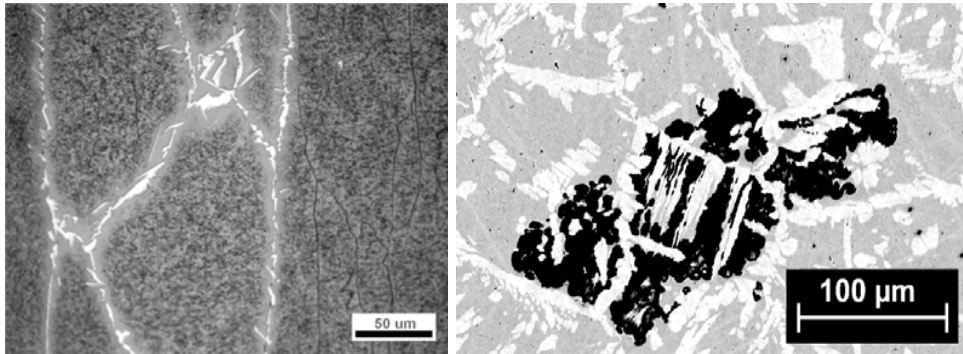
Although nitrogen has a high diffusion rate, the solubility in the ferrite is low and decreases with decreasing temperature. Formation of the most frequently reported chromium nitride  $\text{Cr}_2\text{N}$  may take place in the supersaturated ferrite in the temperature range 700–900°C during rapid cooling or isothermal heat treatment. Nitride precipitation occurs particularly in welds and HAZs with rapid cooling resulting in high ferrite contents. This is particularly the case when laser welding.

The precipitation of chromium nitrides can be reduced by increasing the austenite level by higher heat input or by additions of austenite-promoting elements such as nickel and nitrogen. At higher nitrogen contents, the driving force for austenite precipitation increases and the start temperature for austenite formation is higher; the diffusion required for nitrogen transport to grain boundaries is thus facilitated and austenite formation dominates. Slow cooling rates also reduce the amount of  $\text{Cr}_2\text{N}$  by increasing austenite formation, so nitrogen can dissolve.

Figure 2a shows excessive ferrite content in a 22Cr laser weld with high amounts of  $\text{Cr}_2\text{N}$  precipitates. The presence of  $\text{Cr}_2\text{N}$  precipitates has been demonstrated in many works to decrease the pitting resistance of welds and is due to adjacent depletion of chromium and nitrogen. When present at the surface, chromium nitrides are known to decrease the corrosion resistance, but the nitrides are not as harmful if these are not exposed to the corrosive medium.

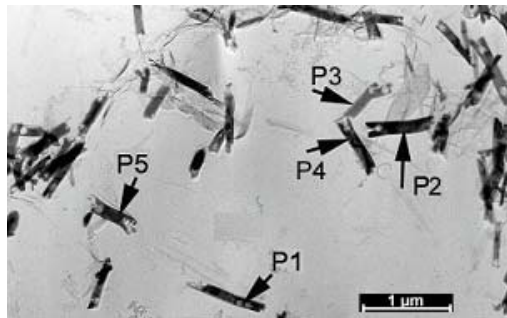
Adjacent to the inter- and intragranular austenite phase a precipitate free zone in the ferrite is observed, which corresponds to the diffusion range of nitrogen during the weld thermal cycle. The nitrogen-depleted regions are the result of the migration of nitrogen into the adjacent austenite during the transformation.

The pitting propagates preferentially within the nitride-rich centres of the ferrite grains and can stop at unaffected grain boundary austenite that has higher corrosion resistance, Figure 2b.



**Fig.2. (a) A highly ferritic microstructure in a 22Cr steel with large amounts of chromium precipitates and ferrite-ferrite grain boundaries. (b) Preferential pitting attack of the ferrite phase in an LDX 2101 weld metal.**

Figure 3 shows Cr<sub>2</sub>N precipitates in a HTHAZ simulated LDX 2101 specimen [B]. The chromium nitride precipitates were more densely distributed in the specimen with a higher cooling rate, which also had a higher ferrite content.



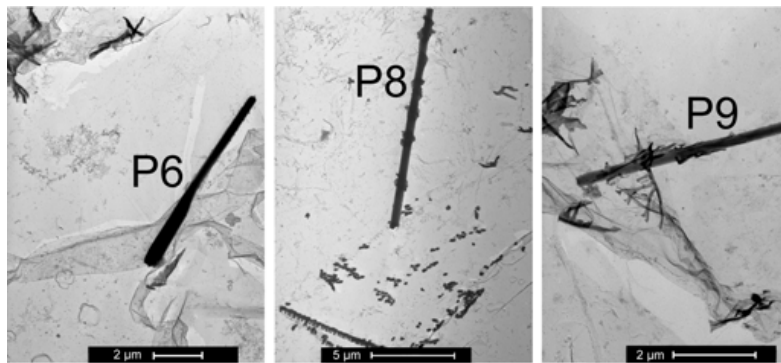
**Fig. 3. (a) Bright field images of the distribution of Cr<sub>2</sub>N precipitates after HTHAZ simulation for 5 s at 1360°C followed by air-cooling.**

### 3.5.2. Titanium nitrides

Titanium nitrides can be found in ferrite grains located in zones with high amounts of chromium nitrides. In Paper B, HTHAZ was simulated for LDX 2101 at different cooling rates. Two types of titanium nitride or carbonitride precipitates, (Ti,Cr,Mn)(C,N), were found; titanium-rich and titanium, chromium and manganese-rich, Figure 4. The (Ti,Cr,Mn)(C,N) precipitates were significantly larger than the Cr<sub>2</sub>N precipitates and more sparsely distributed. No other precipitates were seen in the vicinity of the titanium-rich particles, while chromium carbides precipitated on the more chromium and manganese-rich precipitates.

No chromium nitride precipitates were seen, confirming that the presence of titanium nitrides prevents precipitation of chromium nitrides by depleting the ferrite matrix surrounding it. The cooling rate did not affect the distribution and occurrence of (Ti,Cr,Mn)(C,N) since these are formed during solidification and are thus not sensitive to simulation temperature [B]. The titanium precipitates contain less chromium than the

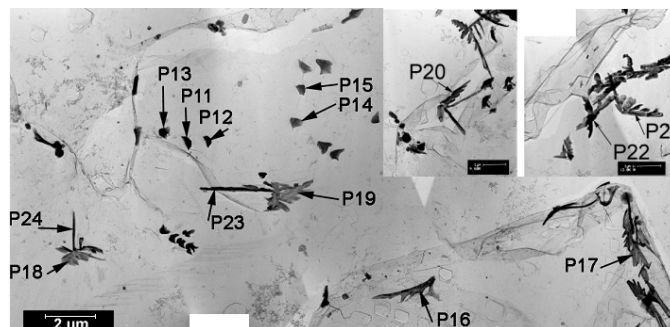
chromium carbides and are sparsely distributed, which make their effect on corrosion resistance less drastic.



**Fig. 4. Titanium nitride or carbonitride precipitates after HTHAZ simulation of LDX 2101 for 5 s at 1360°C followed by air-cooling [B].**

### 3.5.3. Chromium carbides

Small amounts of Cr<sub>23</sub>C<sub>6</sub> grain boundary carbides have been found in simulated HTHAZ specimens. In HTHAZ simulated LDX 2101, chromium carbides of M<sub>23</sub>C<sub>6</sub> type were primarily found in the grain boundaries, Figure 5.



**Figure 5. Bright field images of M<sub>23</sub>C<sub>6</sub> distribution and shape, and diffraction patterns of some of the precipitates found after HTHAZ simulation of LDX 2101 for 5 s at 1360°C followed by air-cooling**

The compositions were slightly different in three observed carbide morphologies; small, elongated, and branched shaped. The smallest precipitates contained some molybdenum, while the elongated carbides had higher chromium content than the branched ones. The occurrence decreased significantly with increased cooling rate and virtually no carbide precipitates were found when water quenching.

Chromium carbides were primarily precipitated along the grain boundaries; hence they do not affect the pitting resistance in the centre of the ferrite grains. As the carbon content is kept low in the modern duplex stainless steels, the amount of precipitates is low and the effect on corrosion resistance is normally negligible.

## 4. Conclusions

The recently-developed lean duplex stainless steel LDX 2101 has here been demonstrated to have good weldability. It can be welded autogenously, even with laser that normally is avoided when welding duplex grades. The mechanical properties of the welds were in parity with the base metal, while the ductility and corrosion performance were marginally lower.

The austenite formation in autogenously welded LDX 2101 was considerably better than what has been reported for other duplex grades. Paper C shows that nitrogen additions to the shielding gas and filler additions increase the austenite formation and make the weld metal more resistant to pitting.

The effect on CPT is small for the GTA welds, but is clearer for the laser welds, where the CPT increased somewhat with austenite content. The pitting resistance of thoroughly cleaned GTA welds was a few degrees centigrade lower than for the base metal and the majority of the laser welds showed similar or somewhat lower pitting resistance.

Formation of a HTHAZ with coarse grains and nitride precipitates of Cr<sub>2</sub>N type may potentially reduce the corrosion resistance and become the weakest region when using filler metal or nitrogen enriched shielding gases.

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