# DUPLEX STAINLESS STEEL. CORROSION RESISTANCE

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**Abstract:** The corrosion performance of the recently-developed lean duplex stainless steel LDX 2101 is higher than that of 304 and can reach the level of 316. This thesis summarises pitting resistance tests performed on laser and gas tungsten arc (GTA) welded LDX 2101. It is shown here that this material can be autogenously welded, but additions of filler metal, nitrogen in the shielding gas and use of hybrid methods increases the austenite formation and the pitting resistance by further suppressing formation of chromium nitride precipitates in the weld metal. If the weld metal austenite formation is sufficient, the chromium nitride precipitates in the heat-affected zone (HAZ) could cause local pitting, however, this was not seen in this work. Instead, pitting occurred 1–3 mm from the fusion line, in the parent metal rather than in the high temperature HAZ (HTHAZ).

Stainless steels are corrosion resistant due to formation of an invisible, 2–4 nm thick, passive film that can naturally be established in oxidising environments when the steel contains at least 12% chromium. This film has the ability to be rebuilt by oxidation of the underlying metal when it has been damaged, i.e. it has self-healing properties. There are, however, environments in which permanent breakdown of the passive layer occur either uniformly or locally, causing corrosion of the unprotected surface.

Uniform corrosion or general corrosion occurs with even corrosion rate over the whole surface that is exposed to the corrosive medium (often a strong acid e.g. hydrochloric acid or hydrofluoric acid). The corrosion rate is generally expressed as the material loss in mm/year and this can thus be used as an estimation of the lifetime. Localised pitting corrosion most often occurs where chloride ions cause a local breakdown of the passive layer. The presence of halides, such as chlorides, in neutral or acidic solutions increases the corrosivity of both organic and inorganic acids. The solution becomes more aggressive at high chloride concentration, low pH and high temperatures, but also small amounts of chlorides may affect the pitting corrosion resistance of stainless steels.

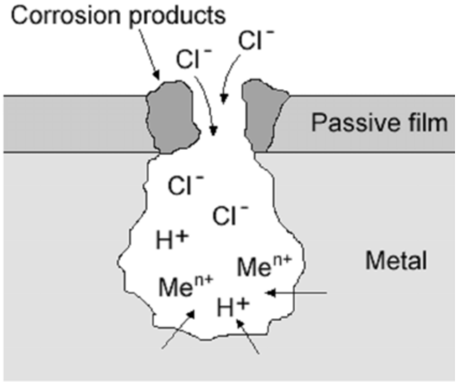

***Fig.1. Cross-section of a corrosion pit.***

The pits often appear to be rather small at the surface, but may have larger cross-section areas deeper inside the metal, Figure 1. Pitting corrosion is often more severe than uniform corrosion due to the rapid propagation rate and it is not possible to circumvent the problem by dimensioning with thicker gauges as for carbon steels. As the attack is small at the surface and may be covered by corrosion products, pitting attack often remains undiscovered until it causes perforation and leakage.

The pitting resistance of the weldment after adequate post weld cleaning is generally somewhat lower than for the parent material. However, there are a number of metallurgical reactions that can occur and the corrosion resistance can be affected negatively by several factors and phenomena. The surface condition is important for the corrosion performance of welded duplex grades. Surface roughness, slag particles, micro-crevices and weld oxide formation can have a decisive influence on the pitting resistance. Precipitates such as sigma phase can also contribute to a loss of the pitting resistance, but these have not been found in any of the LDX 2101 welds examined within the thesis work. Intergranular corrosion previously encountered in older types of duplex steels is no longer of concern in the modern duplex grades with low carbon content. When chromium carbides appear, these are less harmful in duplex grades, since the ferrite allows a rapid healing of depleted zones compared to austenitics.

## 1.Effect of nitrogen on corrosion resistance

Nitrogen is the only element, which simultaneously increases the corrosion properties and the structure stability of the alloy. Nitrogen has a strong beneficial influence on the passivity of stainless steels and is favourable for increasing the resistance of the base metal to chloride-induced pitting corrosion, crevice corrosion, intergranular corrosion and SCC. The impact of nitrogen on the pitting resistance is substantial and attributed to the improvement of the austenite phase. Its estimated that the nitrogen content required for achieving the same pitting resistance in both ferrite and austenite in 22Cr steels is approximately 0.18%. In base metals with lower nitrogen content, the austenite would be less resistant to pitting. Nitrogen is the most important alloying element for improved weldability of duplex stainless steel since it together with nickel causes the formation of austenite to occur at higher temperatures. High nitrogen contents thus decrease the influence of the cooling rate on the microstructure and pitting resistance, and the material becomes less sensitive to welding with low heat inpu.

As indicated by the PRE, nitrogen is important for the corrosion properties and nitrogen loss from the weld pool could consequently lead to a decreased pitting resistance due to high ferrite contents associated with nitride precipitates. Normally the nitrogen loss is negligible when using slag shielded welding techniques such as shielded metal arc welding (SMAW) since the slag layer protects the molten pool from emitting nitrogen. Nitrogen additions of a few percent to the shielding gas when GTA welding has been shown to increase the corrosion resistance of the weld metal for both single and multi-pass welds measured with potentiodynamic polarisation and critical temperature tests. Both the nitrogen content and austenite level in the weld metal are well known to increase with increasing nitrogen content in the shielding gas and to increase the weld metal pitting resistance in the as-welded and heat treated conditions and this is particularly effective when welding without filler such as during autogenous GTA and plasma arc welding (PAW). Nitrogen can also be considered in the backing gas to counteract the degassing of nitrogen from the weld and use of 90% $N_2$ + 10% $H_2$ is frequently recommended to prevent nitrogen loss for optimum corrosion resistance.

There is often a practical maximum limit of how much nitrogen that can be added to the shielding gas. In contrast to austenitic stainless steels, the nitrogen solubility is lower in the solid state so there is a risk of pore formation during solidification. Too high nitrogen levels can result in problems with porosity in the weld metal, especially at high cooling rates where there may be insufficient time for the nitrogen to redistribute by diffusion. When

GTA welding, additions of more than 3% N2 to the shielding gas has been reported to cause severe erosion of the tungsten electrode.

In laser welding, however, nitrogen losses cannot be adequately compensated by nitrogen additions in the shielding gas. Active evaporation of metal during Nd:YAG welding is suggested to further limit the absorption.

Normally, when laser welding; the effect of nitrogen additions to the shielding gas is negligible contrary to GTA welding where nitrogen additions have a large impact on the final ferrite content. Nd:YAG laser-GTA hybrid welding allows, on the other hand, some adsorption of nitrogen from the shielding gas. Matching filler additions have limited effect and pure nickel may be required to reach satisfactory austenite levels in duplex stainless steel during laser welding. A more applicable solution is, however, to use laser-GMA hybrid welding. This results in considerably higher heat input, which has larger effect on austenite formation in LDX 2101 than filler additions. Figure 2 shows the effect of weld metal austenite formation on the pitting resistance of laser welded LDX 2101.

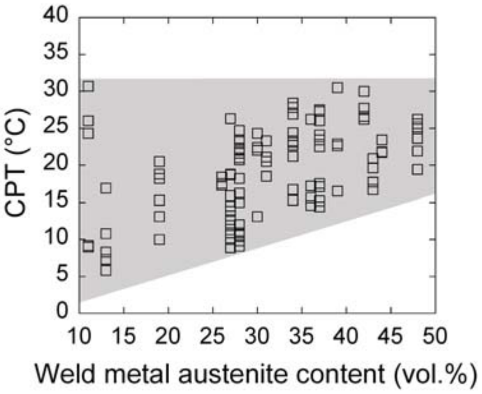

***Fig.2. Influence of laser weld metal austenite content on the CPT (root) for LDX 2101 welds [B]. The austenite fraction varies for different laser methods, when adding filler metal and when using laser-hybrid welding methods [B].***

## 2. Effect of heat input on corrosion performance

Due to its effect on the weld thermal cycle, the heat input has been shown to have a significant influence on the structure and properties of welded duplex stainless steels, and the material producers often specify a suitable heat input range. The corrosion resistance nor the mechanical properties of welded 2205 varied significantly for normal heat input (0.3–2.0 kJ/mm) or for a weld metal ferrite level between 23 and 53%. The cooling rate should, however, be sufficiently slow to prevent high ferrite fractions in the HAZ and sufficient to avoid formation of secondary phases.

In conventional welding, large deviations in phase balance between base metal and as-solidified weld metal can partly be avoided by adding nitrogen in the shielding gas or by using a high nickel filler metal or both. In the HAZ the microstructure can essentially only be controlled by the cooling rate, which is dictated by welding parameters and material geometry.

### 2.1. Low heat input

The cooling rate is primarily related to the heat input and to the material thickness. Low heat input and thick gauges may lead to rapid cooling rate. The consequence of a too low heat input is insufficient time for adequate austenite formation, resulting in highly ferritic microstructures and considerable amounts of nitride precipitates within the ferrite grains in the HAZ and fusion zone, which in turn could have a detrimental effect on corrosion resistance and toughness. Alloys with δ ferrite contents exceeding 80% in the HAZ can have seriously impaired pitting corrosion resistance. PWHT can restore the pitting resistance by improving the austenite formation by elimination of nitrides.

The minimum arc energy to avoid rapid cooling normally is specified to 0.5–0.6 kJ/mm where PWHT is not prescribed, but it must be recognised that the cooling rate is dependent also on material thickness. A thin material can normally be welded with lower heat input compared to a thicker material where the larger amount of surrounding material would contribute to faster cooling. Work in Paper B showed that laser welds in 1 mm thick LDX 2101 with as high ferrite content as 89% had high corrosion resistance, although higher heat input and filler additions improved the pitting resistance of the weld metal.

### 2.2. High heat input

High heat inputs usually result in slower cooling rates. This favours nucleation and growth of austenite and can thus lead to better resistance to localized corrosion of both the weld metal and HTHAZ. Slow cooling rates allow diffusion of ferrite-stabilizing elements such as chromium and molybdenum into the ferrite phase towards the equilibrium values, and this has been reported to increase the corrosion resistance.

Extremely high heat inputs should, however, generally be avoided in order to prevent excessive ferrite grain growth in the weld region that can affect the ductility and toughness. Too high heat inputs may also cause formation of intermetallic phases in the HAZ. Precipitation of $Cr_{23}C_6$ or σ phase can take place when the cooling time is too long. This is rarely a problem in lean or standard duplex grades, but of some concern for the superduplex steels, especially when multipass welding.

Multipass welding can also result in formation of secondary austenite with low contents of chromium, molybdenum as well as nitrogen, and thus somewhat lower pitting resistance.

## 3. Effect of element partitioning on corrosion resistance

As indicated by the PRE, the pitting resistance of a stainless steel is primarily related to the amount and distribution of the elements chromium, molybdenum and nitrogen. Tungsten and copper are other elements with a documented effect on the corrosion resistance. Segregation of important alloying elements in duplex stainless steel welds can consequently locally reduce the corrosion resistance. Element partitioning of particularly molybdenum is known to decrease the pitting resistance of high-alloyed weld metal. This phenomenon is, however, not as prominent as for the austenitic stainless steels, since duplex stainless steels have a ferritic solidification resulting in a lower partitioning of alloying elements.

As duplex weld metals solidify in ferritic mode and the austenite formation occurs in solid phase, the partitioning of alloying elements between austenite and ferrite differs from the base metal and some partitioning of alloying elements occurs during the dendritic solidification. Nitrogen shows normally the largest partitioning in duplex stainless steel welds. It is strongly partitioned in the austenite and is depleted in the adjacent ferrite.

The diffusion range is, however, limited and the central ferrite regions become supersaturated in nitrogen. These regions should exhibit higher pitting resistance according to the PRE value. This is, however, impaired by chromium nitride precipitates, which on the contrary make these regions more susceptible to pitting corrosion. Local chromium and nitrogen depletion around the chromium nitride precipitates may lead to significantly lower PRE than for the ferrite matrix and the chromium nitride precipitates become preferential pitting sites. The element partitioning in duplex weld metals is strongly affected by the composition of the material, but also the heat input plays an important role. At low arc energies nitrogen diffusion controls the austenite formation and the substitutional elements are evenly distributed.

When welding with higher arc energies, the slower cooling rate will allow some diffusion of chromium, nickel and molybdenum. In consequence, depending on arc energy, the composition and corrosion resistance of the ferrite and austenite can vary relatively and the situation is further complicated by subsequent element redistribution during an additional thermal cycle, as occurs in multipass welding.

## 4.Weld oxides and their influence on corrosion properties

During welding, thermal oxide frequently referred to as heat tint or weld discoloration is formed on the surface adjacent to the weld, which has been subjected to temperatures above 300–400°C. The weld oxide is generally considered to be a thermal oxide formed under diffusion control. It has different compositions and is typically several orders of magnitude thicker than the 2–4 nm thick passive film naturally established in oxidising environments on stainless steels.

Weld oxides are formed rapidly and could thus be expected to have a composition, which is far from equilibrium. Surface oxides on stainless steel generally impair the corrosion resistance. The presence of heat tint has been demonstrated to increase significantly the susceptibility to localised corrosion attack compared to parent metal; even invisible oxides can have a detrimental effect. Low-alloyed stainless steels appear to be more sensitive than steels with higher corrosion resistance. The effect of heat tint on pitting resistance has variously been related to the oxide composition, thickness, structure, homogeneity and chromium distribution. These factors are in turn controlled primarily by the bulk composition, peak temperature and oxygen content in shielding and purging gas during welding. Several authors consider that the reduction in corrosion resistance is due to a thin chromium depleted layer located in the underlying base metal and caused by chromium diffusion from the bulk into the chromium-rich oxide.

Others report that they have not found any such chromiumdepleted layer. Auger electron spectroscopy (AES) and glow discharge optical emission spectroscopy (GD-OES) sputter depth profiles have shown that heat tint formed at relatively low temperatures consists primarily of iron due to insufficient diffusion of chromium. The oxide becomes more iron-rich at low temperatures. At intermediate temperatures, chromium-rich oxide forms due to an increased chromium diffusion rate. Chromium dominates in the weld oxide formed at high temperatures and reaches a maximum above 900°C. A more resistant chromium-rich outer layer was formed at higher temperatures and acted as a passive film by forming CrOOH in chloride solutions Although the negative effect of weld oxide on corrosion resistance is well documented, it has also been demonstrated that oxide removal by adequate mechanical and/or chemical cleaning can restore the corrosion properties close to those of the bulk material. Several techniques for removal have been suggested and evaluated; of these pickling has proven to be the most effective method.

The overall conclusion is that weld discoloration has to be removed to maintain the corrosion resistance and that mechanical cleaning followed by pickling gives the best result. Coates reported that surface finish is an important additional factor that influences the resistance to initiation of pitting and possible crevice corrosion. The resistance increases with smoother surfaces. Weld oxides have caused several failures in such steels due to local pitting attack on the root side, initiated by improper post-weld cleaning. This is especially the case for welded tubular products where pickling can be readily performed on the outside surface, but backing gas must be used on the root side to suppress oxide formation. For such joint types, purging with 90% $N_2$ + 10% $H_2$ may give a better result. The presence of heat tint on the weld and HAZ of any stainless steel will lower the corrosion resistance and make the surface more susceptible to pitting and crevice corrosion.

One work has indicated that oxygen contamination in the purging gas should be limited to maximum of 25–50 ppm in order to avoid severe oxidation. The range they specified was from a resistant straw-coloured oxide to susceptible purple and dark blue colours. However, a shiny weld and a straw yellow HAZ are generally regarded as signs of sufficient root protection for adequate corrosion resistance. In most cases it is assumed that weld discoloration on the cap surface is removed, hence the majority of heat tint studies have been performed on weld oxides at the root side.

Only a few studies of heat tint formation on duplex stainless steels have been reported. The CPT of root surface oxides formed on duplex (2304, 2205 and 2507) and super austenitic stainless steels (904L, 254 SMO and 654 SMO) have been compared to low-alloyed austenitic grades. However, weld discoloration on the higher alloyed grades does not affect the corrosion resistance to the same extent as for the lower alloyed grades. The consequence is that the vast majority of studies on heat tint have concentrated on low-alloyed steels. The nickel content of about 5% in the well-established duplex steel 2205 has been partly replaced by manganese and nitrogen in the lean duplex grade LDX 2101.

No studies concerning the effect of manganese on the heat tint formation have been found in the literature, but many papers report manganese present in surface oxide on steel that has been oxidised for longer times in isothermal exposures.

Heat tints formed on the duplex steels LDX 2101 and 2304, welded with and without nitrogen additions to the shielding gas, were studied to determine the effect of base metal and shielding gas composition on the weld oxide by X-ray photoelectron spectroscopy (XPS). Compared to commodity austenitics (300 series) where iron and chromium are dominant in forming weld oxides, lean duplex grades show a relatively strong influence of manganese and nitrogen. Formation of heat tint is normally explained by oxidation of the parent metal and diffusion from the weld metal.

In this work it has been shown that manganese is evaporated from the weld metal and forms weld oxide by subsequent redeposition from the gas phase, Figure 3. Nitrogen additions to the shielding gas enhance evaporation from the weld metal because of the higher weld temperatures attained. This in turn makes the weld oxide thicker due to redeposition and also changed composition of the weld oxide into a double-layer oxide. For LDX 2101 the double-layer oxide was found to consist of manganese oxide and manganese oxynitrides, while on 2304 samples chromium oxynitrides are formed under the outer surface layer consisting essentially of manganese oxide.

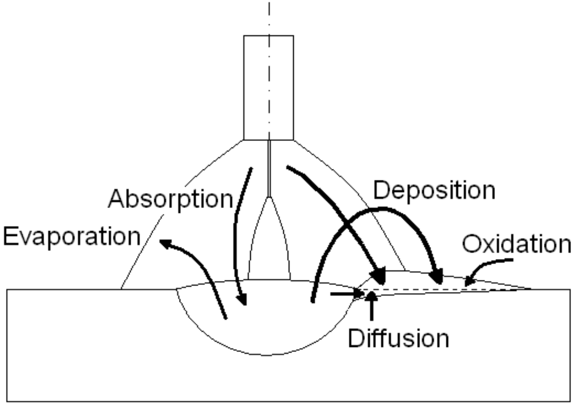

*Fig. 3. Proposed transportation paths involved in weld oxide formation*

When welding with pure argon, manganese oxide dominated on both LDX 2101 and 2304. Nitrogen additions to the shielding gas thus increase the weld metal manganese evaporation and encourage the formation of oxynitrides.

A schematic illustration of heat tint formation on LDX 2101 and 2304 when welding with and without nitrogen additions to the shielding gas is presented in Figure 4. The weld oxide formed on LDX 2101 was thicker and wider than the oxide formed on 2304; and contained more manganese and nitrogen. This difference is considered to be primarily due to the different steel compositions. In LDX 2101 some nickel has been replaced with manganese and nitrogen, while 2304 has both higher nickel and chromium contents.

The fraction of manganese increases and the oxide becomes both thicker and somewhat wider when welding with nitrogen in the shielding gas. This is again related to the absorption-evaporation-deposition process.

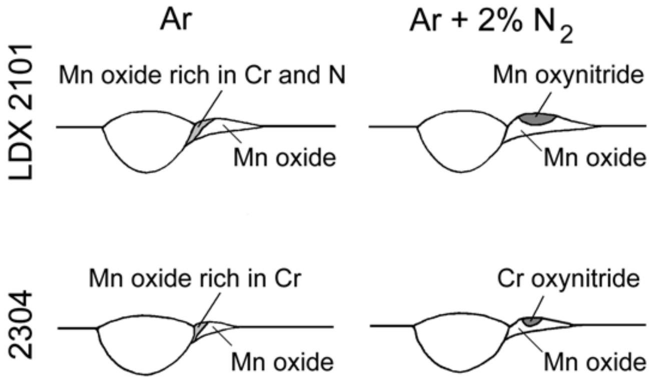

*Fig. 4. Proposed weld oxide composition for LDX 2101 and 2304 welded with and without nitrogen additions to the shielding gas .*

## 6. Discoloration of welds

Four different commercial duplex stainless steel grades (LDX 2101, 2304, 2205 and 2507) were GTA welded bead-on-plate using pure argon and Ar + 2% N2 as shielding gas. A simple corrosion test, in which polished duplex welds were interleaved with damp paper for 10 hours, was used to demonstrate that the composition of the heat tint changes when nitrogen is added to the shielding gas.

The wet paper corrosion test revealed that the composition of the heat tint formed during welding with nitrogen additions to the shielding gas is different from the weld oxide when pure argon is used. The specimens welded with pure argon were unaffected while all duplex materials welded with Ar + 2% N2 displayed stains at different distances from the fusion line after the test, Figure 5.

The reason seems to be manganese or chromium oxynitrides formed in the latter case are responsible for the staining. The distribution of the discoloration corresponds to the region where pitting normally occurs and it has been shown in several works in the literature that this is where the oxide is most iron-rich.

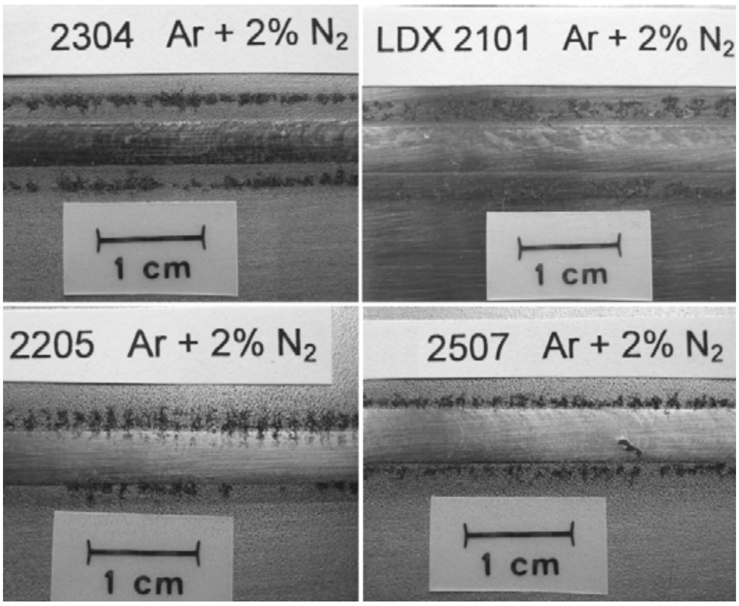

***Fig. 5. Weld discoloration after the wet paper corrosion test***

## 7. Conclusions

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 Cr2N type may potentially reduce the corrosion resistance and become the weakest region when using filler metal or nitrogen enriched shielding gases. This was, however, not seen in this work. Instead, the majority of the pits after corrosion testing on pickled LDX 2101 welds were located in the weld metal, randomly in the base metal or 1–3 mm from the fusion line in the parent metal rather than in the coarse grain zone with chromium nitrides.

Chromium nitride precipitates in the HTHAZ do not seem to be the limiting factor in this case. If the weld metal has sufficient nitrogen content, and hence adequate austenite formation, the weld oxide controls the location of pitting. Consequently, no pitting is found in the HTHAZ. Instead the weld oxide plays an important role. As shown, the heat tint formed on LDX 2101 contains significant amounts of manganese, suggested to be primarily evaporated from the weld metal followed by subsequent redeposition. Nitrogen additions to the shielding gas increased this evaporation.

Oxynitrides were also formed in the weld oxide and these are suggested to cause discoloration when subjected to a wet paper corrosion test. The oxide formed on LDX 2101, when welding with nitrogen-enriched shielding gas, is different from that formed when pure argon is used, but all GTA weldsC showed high pitting resistance after pickling. The ASTM G150 test was unsuitable for measuring the CPT of polished, but not pickled LDX 2101 welds, since the tests failed due to an initially high current peak exceeding the threshold value. No pitting could be seen, but the oxide became locally darker after the test.

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