Corrosion performance of welds in duplex, superduplex and lean duplex stainless steels
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Abstract
To achieve good corrosion resistance in a weld is much more challenging than for plate or sheet material, which has undergone controlled rolling, heat treatment and pickling processes in the steel mill. The choice of weld procedure and parameters, filler metal and shielding gas all play important roles. For duplex and lean duplex grades it is essential to ensure that an adequate amount of austenite is formed in the weld metal and heat affected zone, in order to fulfil requirements in terms of austenite-ferrite phase balance, but also to avoid the precipitation of detrimental phases such as intermetallics and nitrides. In addition, the importance of good post-weld cleaning to ensure good corrosion properties cannot be over-emphasised.

This paper focuses on a number of different examples of pitting corrosion of welds in the duplex grades UNS S32101, S32304, S32205, S82441 and S32750. These illustrate the role of microstructure control to attain good corrosion performance. The effect of residual weld oxides or heat tint in degrading the corrosion performance is also explored, together with evaluation of the degree to which the corrosion resistance can be restored by the use of appropriate pickling processes.

Key words: Stainless, duplex, weld, corrosion, oxide

Introduction
Duplex stainless steels combine a number of attractive features. The two phase microstructure, with approximately equal amounts of austenite and ferrite, imparts a higher strength than the corresponding austenitic grades and a good resistance to stress corrosion cracking. The lower nickel contents of duplex grades, typically in the range 1–7% compared with 8–25% in the austenitic grades also gives cost advantages and better price stability in times of nickel price volatility. In the steel mill, the duplex stainless steels are produced by a very well controlled process of rolling, annealing and pickling in order to impart the optimal properties to the material, whether it be as thick plate, pipe, tube, precision strip or bar.

However, the vast majority of applications require welding, which introduces the metallurgical challenges that heating should not give rise to undesirable phase changes and that a favorable structure must be reformed in a matter of seconds after melting. This applies both to the weld metal, which is melted and can be modified in terms of composition by addition of filler metal, and the surrounding heat affected zone in which there is an imposed heating and cooling cycle on the base material. An indication of the transformations which can occur is shown in the equilibrium diagram in Figure 1. On solidification from the melt, ferrite is formed first, then some of this ferrite transforms to austenite in the solid state. In practice what this means for welding is that an almost fully ferritic weld can be produced if the cooling is very fast so that there is insufficient time for the transformation to austenite to occur. This has the further drawback that nitrogen, which partitions preferentially to the austenite phase, may become trapped in the ferrite where it forms nitrides. This may typically occur if the heat input is low and is typically encountered for laser welds in which the melted volume is small and cools rapidly due to heat loss to the surrounding material. Slower cooling allows time for an adequate amount of austenite to form but should not be so slow as to promote the precipitation of intermetallic phases such as sigma phase or, at lower temperatures, nitrides and carbides.

Figure 1
Equilibrium phases in a 22Cr duplex stainless steel as a function of temperature, calculation using ThermoCalc software with the TCFE5 database.

The microstructural issues to be faced when welding duplex stainless steels are thus multiple and only when a satisfactory microstructure is attained will adequate corrosion properties be achieved. Having said that, however, there is a certain degree of tolerance to the presence of minor amounts of precipitated phases before the corrosion performance is affected.
Materials

The materials investigated in this work were five duplex stainless steels spanning a wide range of alloying levels and thus corrosion resistance. Because a number of different heats were used for the various welds, the typical compositions are given in Table 1. All materials were in the mill annealed + pickled condition with 2B or 2E surfaces. Also included in Table 1 are the Pitting Resistance Equivalent (PREN) values. This is here defined as $\text{PREN} = \%\text{Cr} + 3.3\%\text{Mo} + 16\%\text{N}$ and is a rough predictor of the localized corrosion resistance for a stainless steel in the perfectly annealed state with a good surface finish. The focus of the present work is on the corrosion performance of sensitised materials and welds. For details of the welding processes per se reference is made to the quoted data sources.

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Table 1. Typical compositions of the duplex stainless steels alloys investigated

Results & Discussion

Critical pitting and crevice corrosion temperatures for the duplex base materials are shown in Figure 2. Good correspondence is actually seen between the G48E and G150 CPT values, although the former are a few degrees lower and the difference becomes more pronounced at higher alloying levels. The CPT for the lean duplex S32101 is 15°C in G48E and in the range 15–20°C in G150, while the corresponding temperatures for the highest alloyed S32750 were 65°C for G48E and 80–85°C for G150. The two can never be used interchangeably.
If duplex stainless steels are subject to slow cooling, as may occur in conjunction with welding with a very high heat input, or inappropriate heat treatment in the temperature range 300–1000°C (300–800°C for the leaner duplex grades) microstructural changes, including precipitation of secondary phases and 475°C embrittlement, can occur. This is illustrated in Figure 3 which includes typical microstructures after longer heat treatment times. The effect of holding times of 1, 10 or 30 minutes at either 850°C or 700°C on pitting corrosion resistance is shown in Figure 4. This indicates that a slight drop in CPT occurs after only 1 minute at 850°C for the standard duplex S32205 and the superduplex S32750, with an appreciable decrease occurring after 10 minutes at this temperature. Scatter bands have been omitted from the figure for clarity, but are detailed in [1]. The grades S32304 and S32101 are largely insensitive to heat treatment in this temperature range, because their leaner alloying concept means that they are remarkably resistant to precipitation of intermetallic phases. However, they do show some decrease in CPT as a result of holding times at 700°C, where precipitation is dominated by nitrides and carbides which can form in the phase boundaries.

**Figure 3** Precipitation kinetics for duplex grades evaluated as the conditions required to give a 50% reduction in impact toughness, and microstructures illustrating intermetallic phases, predominantly sigma phase, and carbides/nitrides

**Figure 4** Effect of holding time at 700°C or 850°C in decreasing the CPT compared to that of the base material. 700°C is the more detrimental temperature for the lean grades S32101 and S32304 while 850°C has a larger influence for the standards S32205 or the superduplex S32750
In a welded structure, as opposed to a base material which has been sensitized to provoke the type of precipitation which can occur in association with welding, the basic phase morphology is also altered. Since the weld is fully ferritic on solidification from the melt, austenite is reformed at the ferrite grain boundaries and as Widmanstätten austenite in crystallographic orientations within the ferrite grains, as illustrated in Figure 5. There is a difference in composition between the austenite and ferrite phases: the former is enriched in nickel and nitrogen and the latter in chromium and molybdenum, and this means that there is usually some difference in corrosion resistance between them. This is also illustrated in Figure 5, in which it is seen that pitting has preferentially occurred within the ferrite phase.

Results from a series of CPT measurements on GTA welds in the five duplex grades are shown in Figure 6, based on data taken from [3, 4]. This shows a number of interesting trends. Firstly, the as-welded CPT is between 20 and 40 °C below that of the corresponding base material, with the result that no as-welded CPT can be determined for the lean duplex grades S32101 and S32304. The larger drop is seen when argon is used as a shielding and backing gas, but this can be mitigated by using nitrogen-containing shielding and backing gases. The primary reason is that nitrogen per se improves pitting corrosion (as seen in the PREN formula) and promotes reformation of austenite to give a more advantageous phase balance. However, pickling the welds to remove the very slight amount of weld oxide can almost restore the CPT to the same level as that of the unwelded base material, if nitrogen shielding is employed.

An even more demanding welding process is spot welding, because the low heat input and thus rapid cooling can give a very ferritic weld. Figure 7 using data from [5] shows how a drop of around 15 °C in CPT occurs as a result of resistance spot welding thin sheets of duplex steels. In the case of the lean duplex S32101, however, this could be restored to a similar level as the base material by the use of a protective argon atmosphere to minimize the oxidation of the spot weld. This was particularly notable since the weld microstructure was far from optimal, with a high ferrite content of 75–85% and some nitrides present in the microstructure. The austenite formation was somewhat lower for the other two duplex grades, S32304 and S2205, due to the lower nitrogen contents in these grades.

Figure 5 Typical pitting in a 22Cr duplex weld, showing how ferrite phase is attacked while austenite remains more resistant [2].

Figure 6 Critical pitting corrosion temperatures according to ASTM G150 for the root side of single-side GTA welds on 1 mm material with argon as both shielding and backing gas or with Ar + 2% N₂ as shielding gas and 90% N₂ + 10% H₂ as backing gas, based on data from [3, 4].

Figure 7 ASTM G150 critical pitting temperature for spot welds in three duplex grades. The beneficial effect of using a shielding gas is apparent for S32101 and gives a CPT on a par with the base material, in spite of the presence of nitrides in the microstructure, based on data from [5].
The corrosion performance of a number of welds in the lean duplex grade S32101 are shown in Figure 8, based on data from [6,7]. In each case the base material CPT is given as a reference point; this shows some variation because of the different surfaces and product forms tested. All welds were pickled prior to corrosion testing, attempts to test the GTA welds with residual weld oxides caused the CPT measurement to terminate just after the starting temperature of 0 °C due to oxide dissolution but no pitting. The figure shows that in the majority of cases the weld CPT was close to that of the base material. This even applies to autogenous welds, where there is no filler metal added to adjust the weld composition. Adding nitrogen via the shielding gas could have a beneficial effect on the weld microstructure, as is illustrated in the microstructures, but for the autogenous GTA welds was found to have only a minor influence on the CPT, increasing it from 15 to 17 °C. Even most laser welds showed acceptable CPT values, above the normally specified minimum of 15 °C for base material. The exceptions were the fiber laser weld in 2 mm material and the Nd:YAG laser weld in 1 mm material, but in both cases a switch to hybrid welding with leading GTA or GMA gave a significant improvement.

**Figure 8** Critical pitting temperatures for various welds in the lean duplex grade S32101, based on data from [6,7]. These include GTA and Nd:YAG, CO₂ or fiber laser welds which were either autogenous (A) or with a filler (B = W 23 7 N L, C = W 22 9 3 NL or G 22 9 3 NL). Micrographs show a reduction in the amount of surface nitride for GTA welds with Ar + 2% N₂ (lower photograph) compared to pure argon (top) but little difference in CPT. The lower CPT values (circled) were improved by hybrid welding.
Conclusions

Results presented in this paper have demonstrated that excellent pitting corrosion resistance, on a par with that of the base material, can be achieved for welds in duplex stainless steels. A critical factor is the removal of weld oxide by pickling, or minimization of oxidation by efficient use of shielding and backing gas. Nitrogen additions to the shielding gas can also have a beneficial effect on weld metal pitting resistance by increasing the weld metal nitrogen content and promoting austenite reformation. The high nitrogen content of the lean duplex steel UNS S32101 means that good corrosion resistance can be achieved even in autogenous GTA welds, laser welds and resistance spot welds.

References


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