



## FUNDAMENTALS ON WELDING OF DUPLEX / SUPER DUPLEX STAINLESS STEELS

Achilles G. Koutlis  
Lead Welding Engineer  
Saudi Aramco, Consulting Services Dept.  
Materials Engineering Division  
Al Midra Tower, Midra Access Rd  
Dhahran, Eastern province, 34481  
Kingdom of Saudi Arabia

Tariq A. Al-Ghamdi  
Engineering Consultant - Welding  
Saudi Aramco, Consulting Services Dept.  
Materials Engineering Division  
Al Midra Tower, Midra Access Rd  
Dhahran, Eastern province, 34481  
Kingdom of Saudi Arabia

Maslat S. Al-Waranbi  
Group Leader - Materials  
Saudi Aramco, Consulting Services Dept.  
Materials Engineering Division  
Al Midra Tower, Midra Access Rd  
Dhahran, Eastern province, 34481  
Kingdom of Saudi Arabia

### ABSTRACT

This paper aims at providing general guidelines for welding duplex stainless steels. Whilst industry practices and literature were reviewed, the document is mainly based on the personal experience of the authors with duplex welding in Saudi Aramco and other projects they had participated during their welding engineering career. If the intent of those explained in this paper is understood and soundly applied, it could be of help to construction Contractors and Fabricators / Manufacturers with ensuring sound quality of weldments and high reliability of the assets they build for their Clients.

Duplex stainless steels are readily weldable provided the involved personnel has knowledge of how the metallurgy works and owns thorough understanding of the particularities in terms of the potential risks during welding and, the associated dos and don'ts.

Key words: Duplex stainless steel welding, Superduplex, ASTM A923 Method C

## OVERVIEW OF THE DUPLEX STAINLESS STEELS

Duplex stainless steels (DSS) are designed to have a balanced microstructure consisting of approximately half austenite ( $\gamma$ ) and half delta-ferrite ( $\delta$ ). The ferrite content in the phase balance may typically vary from as much as 35 to 60% and still obtain the properties those materials are intended for. Duplex microstructures with an approximately equal fraction of ferrite and austenite offer the optimum combination of corrosion resistance and mechanical properties compared to the steels owing only one of the two phases – i.e. the purely austenitic stainless or the ferritic steels. In that aspect, respecting the proportions, DSS are stronger than austenitic stainless steels but not as tough at lower temperatures and they are tougher and more resistant to corrosion than carbon steels but not as strong.

Stainless steels of the duplex family are designed to provide higher resistance to pitting corrosion and corrosion stress cracking in chloride-containing media and significantly higher strength than the standard austenitic stainless-steel grades such as, for instance, Types 304 or 316. The phase balance plays a role and, generally speaking, steels within the material group with higher ferritic content may show lower toughness and elongation whereas lower ferrite fractions may increase the susceptibility to chloride stress corrosion cracking (Cl-SCC).

The main difference in chemical composition, when compared to austenitic stainless steels, is that the duplex have higher chromium content (20 - 28%), higher molybdenum (up to 5%), lower nickel (below 8%) and about 0.05 - 0.5% nitrogen. Depending on their chemistry (primarily, the Cr content) and PREN, steel grades of the duplex family are generally grouped in four categories:

- Lean Duplex: Lower Ni content (1-3%wt) and lower Mo (0.1-0.6%wt), PREN between 21-27. Particular Mo-containing lean duplex (Mo within 2-4.5%wt) have a PREN of 27-34. Characteristic grades, wrought: UNS S32202, S32304
- Standard Duplex: Typical %wt composition of 22 Cr, 5 Ni, 3 Mo, 0.15-0.18 N, typical PREN values in the range of 33-35. Characteristic grades, wrought: UNS S31803, S32205, cast: UNS J92205.
- Super Duplex: Typical %wt composition of 25 Cr, 5-7 Ni, 2-4.5 Mo, 0.2-0.25 N, typical PREN values in the range of 38-41. Characteristic grades, wrought: UNS S32750, S32760, S32550, cast: UNS J93404, J93380.
- Hyper Duplex: 27%wt Cr, higher Mo and N content, PREN at 49 or 50 – e.g. UNS S32707.

Figure 1 shows the typical dual microstructure of duplex stainless steels, with the austenite and ferrite bands.

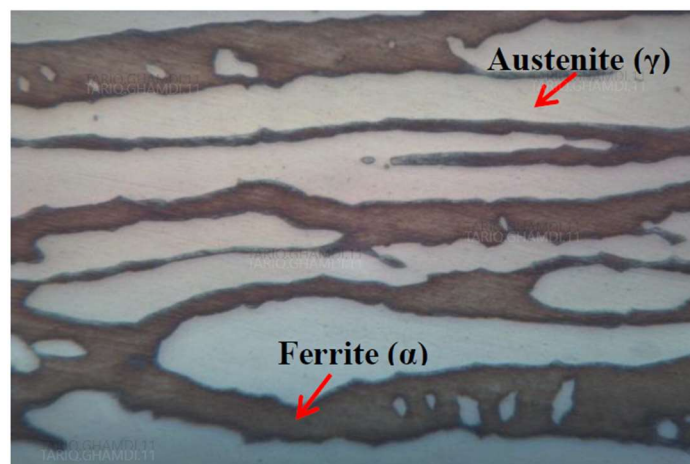


Figure 1: Duplex structure showing the dual phase structure (light bands austenite and dark bands ferrite) – *Maverick Testing Laboratories, Inc. [2]*

## FUNDAMENTALS OF THE METALLURGY OF DUPLEX STAINLESS STEELS

In all iron-containing steels what is physically realized as “rust” is the oxidation of iron. In a simple iron-carbon alloy, iron reacts with the oxygen from the surrounding environment forming an iron-oxide film that is “active” – this meaning, once it forms on the material’s surface, it makes it easier for more of it to form hence, in essence, accelerating corrosion. This reaction is possible to be prevented when chromium is added to the material’s chemistry yet, it must be in adequate quantity. In a simplified manner, chromium at the surface of the material has a greater affinity than iron to combine with the oxygen available in the atmosphere forming a chromium-oxide film instead. When the chromium content in the matrix is above a critical concentration of roughly 10.5%, the chromium-oxide compounds are stable enough to remain on the surface of the material as an inert film impeding iron to react with oxygen. We call this layer “passive” because it acts as a shield, impeding iron oxidation or, equally, atmospheric corrosion. Cr is the primary element responsible for the corrosion resistance of all the stainless steels in general. In principle, the higher its concentration above the tipping value of 10.5%, the higher the corrosion resistance of the steel and this is no exception to the duplexes.

Chromium is a ferrite-stabilizing former. The addition of this element promotes the formation of body-centred cubic (BCC) crystal structure of iron and, also, intermetallic phases. The higher Cr content will increase stability of the ferritic portion of the microstructure with all the benefits that come with it (i.e. resistance to corrosion and chloride-stress corrosion cracking etc.) but, on the other hand, the challenges too – e.g. availability of more sites for chromium carbide precipitation at high temperatures and, higher tendency to formation of intermetallic phases like sigma or chi at shorter time periods. This should be kept in mind when welding these steels. Typically, when chromium increases in the chemistry, the content of nickel and other stabilizing elements needs to increase too to be possible for adequate austenite to form.

Molybdenum is an effective constituent against pitting and crevice corrosion and its boosts resistance three (3) times as much compared to Cr as it could be shown from the classical PREN equation. Of course, this doesn’t come without a price since Mo promotes the formation of intermetallic phases which, on their turn, could have a detrimental effect on the corrosion resistance and toughness hence, it is usually restricted to less than about 5%wt in DSS grades.

Molybdenum is a ferrite former like chromium thus, during welding, molybdenum is susceptible to segregation of its content into the ferritic phase leaving the austenitic regions of the microstructure locally denuded of it. Microsegregation of Cr and Mo is a reason for localized reduction of the corrosion resistance of the DSS welds that often manifests itself through failure to meet requirements for corrosion testing set in the various international standards or test specifications. Lower temperatures for corrosion testing of welds with respect to parent materials permitted in the specifications of some operating companies is the acknowledgement or recognition of exactly this probability for localized segregation of those elements in the as-deposited weld metal and their result in slightly lower corrosion resistance. Again, because Mo is a ferrite former, austenite-promoting elements (like nickel and nitrogen) are typically added in higher quantities to maintain the phase balance.

Although DSS grades are corrosion and oxidation resistant, they cannot be used at elevated temperatures because of the precipitation of embrittling phases in the microstructure at relatively high temperatures. As a consequence, the material properties section of the ASME Boiler and Pressure Vessel Code (BPVC-II-D) restricts the service temperature of all DSS grades to 316°C (600°F). Temperature limits for DSS/SDSS applications in the O&G industry typically range from -50 °C to +300°C.

Contrary to what happens with austenitic stainless steels, duplex stainless-steels solidify first as ferrite in dendritic or cellular mode, which then partially transforms to austenite as the temperature continues to

drop. It is very important to remember this when attempting to weld materials from the duplex family. This shift in the steel's microstructure during cooling happens because of nickel and nitrogen, both of which are strong austenite stabilizers therefore, they promote the transformation of the ferrite's body-centred cubic (BCC) crystals to the austenitic face-centred cubic structure (FCC), raising the steel's toughness. A few other things that should be kept in mind when we are going to talk about welding later on is that both of those elements also delay the formation of detrimental intermetallic phases yet, nitrogen's effect is incomparably higher than nickel's in this regard. In particular for nitrogen, increasing its content in the alloy's chemistry raises the transformation start temperature and increases the rate of the ferrite to austenite transformation [3]. In other words, the more the nitrogen, the more the austenite that will transform from ferrite because the transformation during cooling begins earlier, from a higher temperature.

However, compared to a fully ferritic structure, as the amount of austenite in duplex grades increases, the toughness increases but the strength decreases, the corrosion resistance improves yet, vulnerability to chloride stress corrosion cracking (CI-SCC) increases. As shown in figure 2, adding adequate nickel to a ferritic chromium stainless steel turns it to an austenitic chromium-nickel stainless steel. Yet, smaller additions lead to a duplex structure, a mixture of austenite and ferrite.

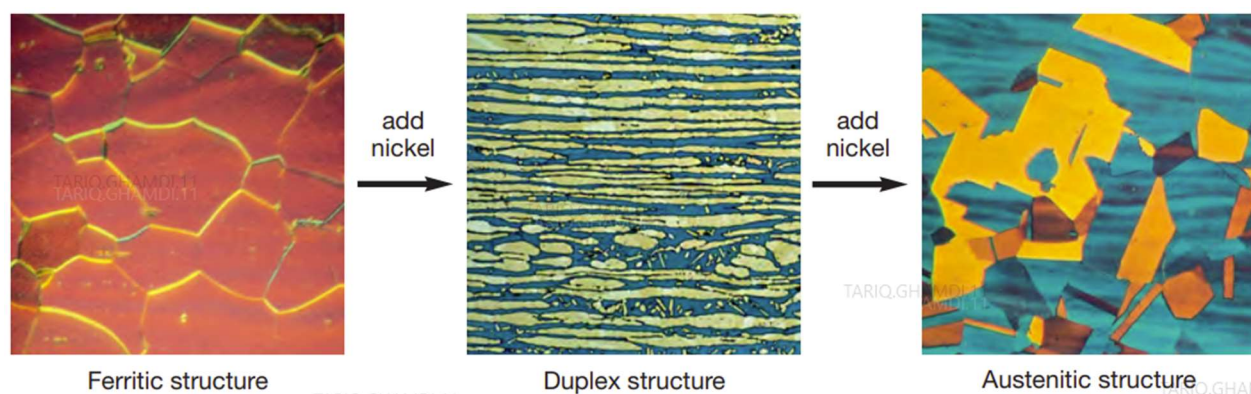


**Figure 2: Effect of nickel content addition on the formation of different microstructures [3]**

The lower nickel content, the higher resistance to CI-SCC and the higher strength compared to austenitic stainless steels, as well as the higher toughness and corrosion resistance compared to carbon steels, open a great portfolio of applications for the duplex grades in more cost-effective ways with respect to the alternatives available by other material chemistries.

The classification of the DSS alloys – i.e. lean, intermediate (22%Cr) and super duplex (25%Cr) grades – is principally based on the alloying level as demonstrated in the beginning of the document but, also, in terms of the Pitting Resistance Equivalence Number (PREN), which is a measure of the resistance to pitting corrosion. PREN is calculated as [1]:

$$\text{PREN} = \% \text{Cr} + 3.3 \times \% \text{Mo} + 16 \times \% \text{N}$$

$$\text{PREN}_w = \% \text{Cr} + 3.3 \times (\% \text{Mo} + 0.5 \times \% \text{W}) + 16 \times \% \text{N}$$

Although N comes into very small quantities in the base metal yet, it has a significant impact on the PREN. The modified PREN formula ( $\text{PREN}_w$ ) acknowledges the role of Tungsten (W) in the corrosion resistance and may be used for some W-containing grades.

Typically, duplex steels have PREN values above 30 but less than 40 whereas this value for super duplex varies between 40 and 45. Higher duplex grades like hyper duplexes (27%Cr – i.e. UNS S32707), own

higher Mo and N contents and PREN above 45, whilst the lean grades typically have lower nickel (1-3%wt), low Mo content (0.1-0.6%wt) and PREN between 21-27 hence, lower cost. Particular Mo-containing lean duplex (Mo within 2-4.5%wt) have a PREN of 27-34. [2, 4]

## WELDABILITY OF DUPLEX STAINLESS STEELS & PRECIPITATION OF DETRIMENTAL PHASES

Serious challenges due to corrosion failures of improperly welded DSS grades have been encountered in the oil and gas industry and Saudi Aramco had been no exception to this. The weldability of all grades of the duplex family is generally better than those of the ferritic stainless steels yet, not as good as that of the austenitic stainless steels. Secondary, brittle, intermetallic phases that reduce both, their toughness and corrosion resistance, may form not only in the parent metals due to the application of incorrect heat treatment procedures at their manufacturing stage but, also, at the weld metal and the heat affected zone (HAZ) when inappropriate welding techniques are employed during fabrication. The main intermetallic phases that could precipitate and could be detrimental to weld deposits and associated HAZ are sigma, chi, chromium nitrides, and alpha prime. Whilst the precipitation of sigma, chi and chromium nitrides occur in a matter of minutes when the temperature reaches specific ranges, alpha prime takes significantly longer time to form hence, it is more of a concern during the materials manufacturing process rather than during welding fabrication unless the welded joints are stress relieved – i.e. in carbon steel vessels with DSS cladding. It is important to know that once they form, intermetallic phases can only be removed by solution annealing and subsequent water quenching.

Microstructure of a 2205 sample aged at 850°C for 40 minutes. The ferrite phase shows darker than the austenite. Sigma phase precipitation appears as black lines at the austenite/ferrite grain boundaries.<sup>(3)</sup>

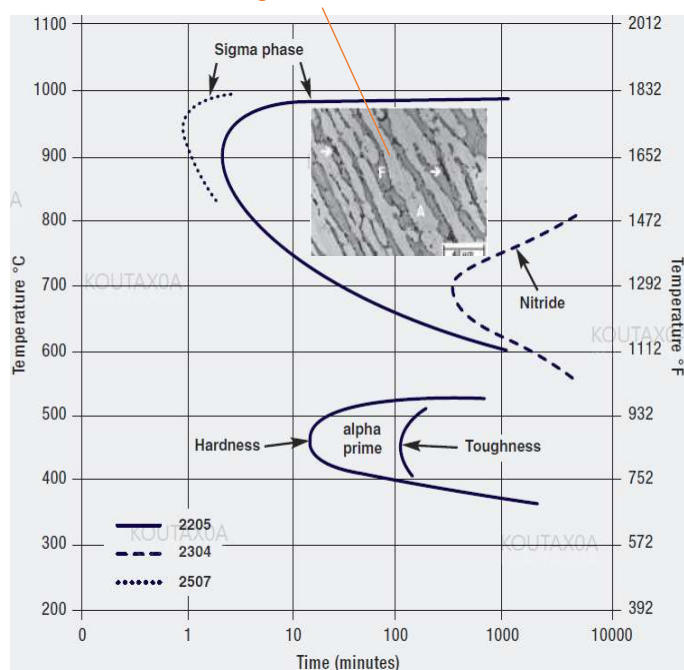


Figure 3: Isothermal precipitation diagram (TTT) for grade 2205 DSS, annealed at 1050°C. Sigma and Chromium Nitride phase precipitation curves for grades 2507 and 2304 are shown for comparison - International Molybdenum Association (IMO), *Practical Guidelines for the Fabrication of Duplex Stainless Steel*, 3rd edition, 2014, London-UK

IMO's publication on DSS [3] and imprints TTTs for 2304 lean duplex (23%Cr but Mo-free), 2205 standard duplex (22%Cr, 3%Mo), and 2507 super duplex (25%Cr, 4%Mo). Note that lean DSS 2304, that

Sigma is the depletion of Cr and Mo at the ferrite austenite interfaces in the form of precipitates generally described as  $M_{23}C_6$  type carbides (i.e.  $Cr_{23}C_6$ ). The result of sigma phase formation is the local reduction of the corrosion resistance (pitting resistance) at the chromium and molybdenum-denuded areas next to the precipitates. Typically, sigma phase forms at temperatures between 570°C and 1000°C and in a short period of time. The phenomenon is more intense in the temperature range of 950-800°C where, depending on the exact chemistry, it may start building up in minutes or, sometimes, in less than a minute (see 2507). Sigma has a tetragonal lattice structure, with the least number of slip planes compared to other lattice structures (i.e. BCC, FCC). It is therefore very brittle and hard with a direct effect on the overall toughness and ductility of the component it may form at – i.e. parent metal, weld deposit or HAZ.

Figure 3 shows the time-temperature-transformation (TTT) curves for three characteristic duplex grades, all plotted in one diagram for comparison of the temperature and time ranges various intermetallic phases form for each grade. The graph was taken from