Sigma phase: a metallurgical challenge when welding duplex

While high strength was the focus of alloy development for many years, today a range of other properties are also essential[1]. Examining new types of failures and metallurgical aspects, especially during manufacturing processes requiring high temperatures such as welding and heat treatment, have led researchers to realise that high strength alone is not sufficient to meet the requirements for a reliable component. Instead, a range of material properties is needed, including toughness, stiffness, hardness, ductility, and corrosion[2, 3, 4].

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Duplex stainless steels (DDSs) consisting mainly of Cr, Ni, Mo and N, are widely used in the market. Duplex grades can be divided into three subgroups: lean duplex, standard duplex, and super duplex. The most common alloys for each of these three subgroups are 2304, 2205 and 2507 respectively. Since the early 1980s, DSS alloys have been commonly used in marine applications, petrochemical industries and oil refineries[5].

The microstructure of duplex is an almost 50:50 mix of austenite:ferrite at room temperature, although commercial alloys may have ratios of 40:60 (Figure 1).

Duplexes possess a combination of high strength and corrosion resistance not readily attained in conventional single-phase austenitic or ferritic stainless steel. Compared to austenitic stainless steels, they have higher corrosion resistance, especially against pitting and stress corrosion cracking (SCC)[3, 6]. Compared to ferritic stainless duplexes offer improved formability, weldability and toughness.

Although the welding metallurgy of these alloys is relatively well understood, heating DSS to high temperatures (450 to 1200°C) is challenging for end-users due to the formation of hard phases such as sigma (σ), chi (χ), intermetallic phases and varies chromium carbides[7] (Figure 2). These phases are often harmful, for example, enhancing embrittlement and reducing corrosion resistance. Besides the reduction in toughness, these also cause intergranular, pitting and stress corrosion cracking.

The heat created during welding of DSS may cause detrimental phases to appear. Various precautions may help prevent this:

- A filler material with 2-3% higher nickel content than the substrate, such as ER2307 and ER2209
- An inert gas environment can increase pitting resistance of the weldments[6]

Heating duplexes to high temperatures (welding, hot working, heat treatment) causes σ phase precipitation. According to the eutectoid reaction - solid to another solid phase transformation, this change mainly occurs at the intersection of three grains and at the grain boundaries between ferrite and austenite - into a lamellar eutectoid structure of σ and secondary austenite γ: delta ferrite $\delta \rightarrow + \gamma$.

The formation of χ phase in DSS is often initially favoured. However, because χ phase may transform into χ phase following further ageing, the χ phase formation is favoured over longer ageing periods.

Based on the Time-Temperature-Transformation (TTT) diagram for DSS, there is a threshold time required to precipitate the intermetallic and hard phases. This time depends on the temperature and chemical composition of the alloy. In the worst-case scenario, the formation of σ phase, which takes place around 900-1100°C, takes around 2 minutes. Fast cooling by quenching in water or oil is therefore advisable. However, quenching often leads to distortion and cracking, particularly with thin components.

Solution annealing (heating to around 1050°C for the appropriate time) followed by air cooling can be an alternative for the quenching process for workpieces less than 10mm thick. Figure 3 shows that the microstructural changes of 12mm thick super duplex 2507 can be recovered to the original microstructure through air-cooling after applying solution annealed treatment from 1100°C.

In the last few decades, numerous studies have investigated the negative

Figure 1. Microstructures of a: 2304, b: 2205, c: 2507. Light is austenite γ, dark is ferrite α.

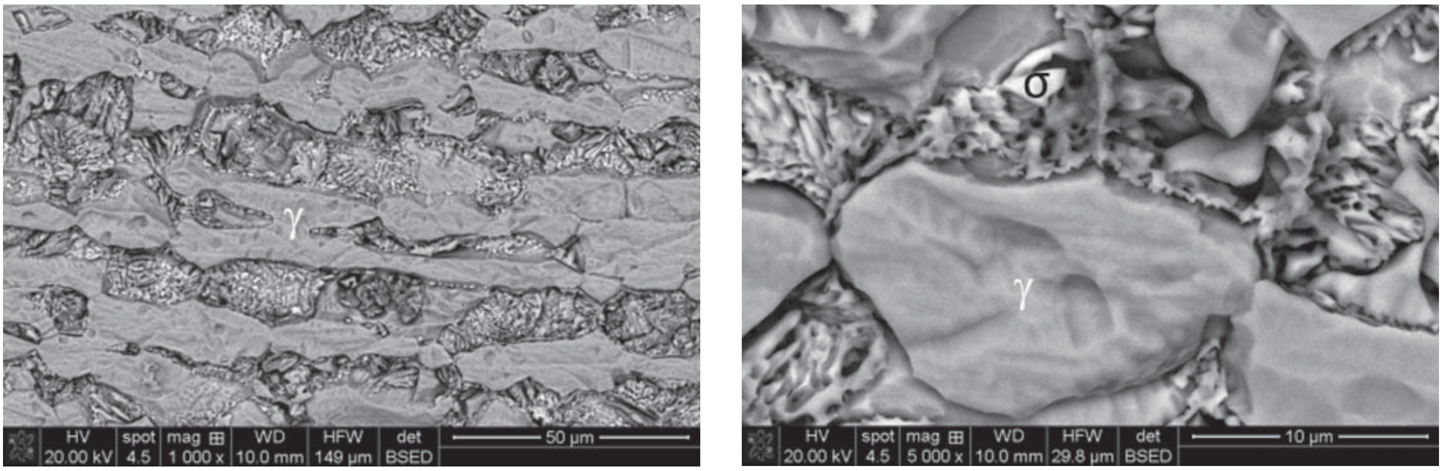

Figure 2. Sigma phase formation of 2205 alloy heated for 10 min at 900°C.

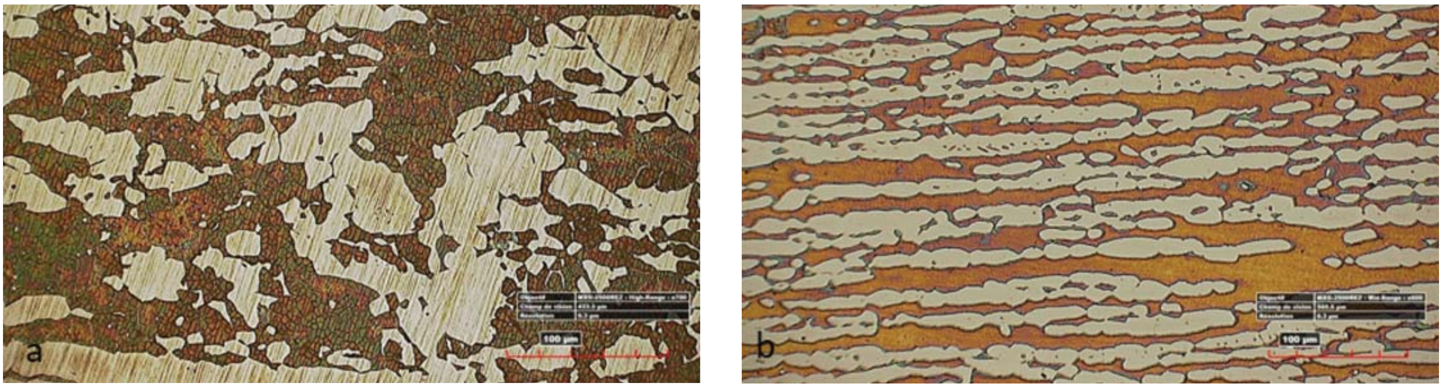

Figure 3. Microstructural recovery, a: heat-treated at 750°C for 1hr, b: heat-treated at 1050°C for 1hr (both air-cooled).

impacts of welding on the mechanical properties of DSS, particularly on toughness and corrosion resistance. The modifications are always referred to as the metallurgical aspects that occur in the fusion zone and HAZ. However, because these two zones are relatively narrow and present intermixing (Figure 4), finding an accurate contribution of each zone on the whole alloy is difficult and always a point of discussion. Figure 4 shows that in the welded zone, due to high temperature and subsequently fast cooling, most of the structure is ferrite content. However, the HAZ is a combination of both phases, γ and α; it can be σ too but this does not appear in low magnifications.

Investigation techniques

Different techniques and methods are available to investigate the metallurgical aspects of heating DSS alloys, including:

- Metallographic and chemical analysis
  Using electronic microscopes, SEM, TEM, EDX, x-ray diffraction and spectra. The metallographic images and chemical composition analysis of specific grains/phases help to recognise specific phases, e.g. σ (Figure 2). However, this is not sufficient to reveal all details about the effect of temperature on the microstructural changes.
- Thermal simulation techniques
  This method can help to characterise the subsequent changes of the microstructure at specific temperatures which have similar heating and cooling rates to the welding process. Applying the heat on samples at conditions similar to the welding situations, but below the melting point, i.e. for HAZ. as the equipment is not capable to record the temperatures of molten materials[4].
- Thermoanalytical Analysis
  Various thermoanalytical techniques are used to detect the metallurgical changes such as σ phase formation. These include magnetic force microscopy, equilibrium thermodynamic conditions, simultaneous

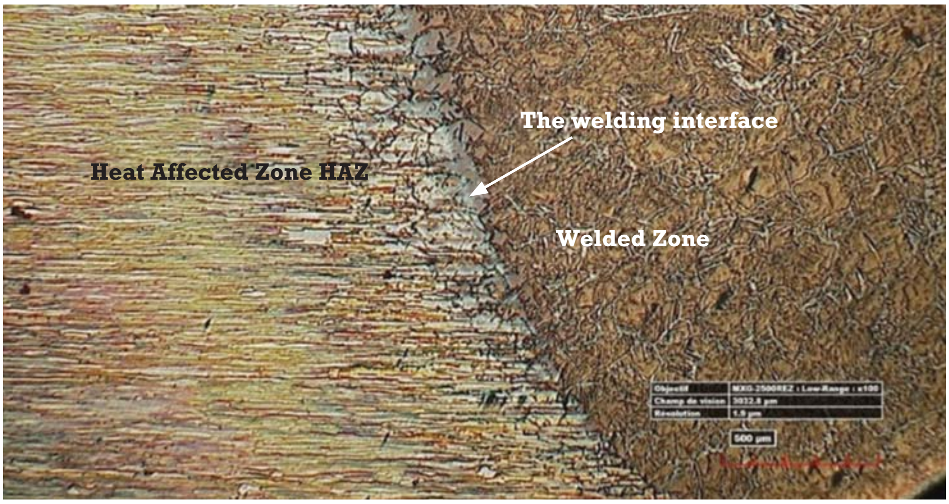

Figure 4. The interface between the welded zone and HAZ of TIG-welded 2205 alloy.

high-temperature thermogravimetry, isothermal drop calorimetry, isothermal dilatometric, differential thermal analysis (DTA) and differential scanning calorimetry (DSC). These techniques measure the difference in the amount of heat required, enthalpy increments, dimensional variation, magnetic flux rate, etc of a sample and a reference material.

Summary

Heating, due to welding or heat treatments, above 500°C causes microstructural changes in DSS. Besides changing the 50:50 balance ratio of austenite: ferrite, hard phases such as sigma are formed at specific temperatures. Solution annealing, even by air cooling from 1050°C, can lead to recovery of the original microstructure. Different techniques, based on heat enthalpy, movement or atoms, dimensional changes, etc can be used to detect sigma phase in DSS alloys.

References

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Full reference list available on request.