THE EFFECT OF COOLING MEDIUM ON THE AUSTENITE-FERRITE EQUILIBRIA OF HEAT-TREATED DUPLEX STAINLESS STEELS

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Abstract

The decomposition of δ-ferrite to austenite has been studied in SAF2205 by using optical and electron microscopy. Heat treatment was conducted at varying temperatures and the effect of temperature on the microstructure was systematically investigated, while the cooling method was also considered as variables. It was found that the maximum amount of austenite occurs at 850°C

and the precipitation of sigma phase in ferrite occurs at 980°C. Chemical analysis showed that Cr and Mo partition to the ferrite and Ni and Mn to the austenite. The results were compared with those obtained from calculations based on thermodynamic data, and it was found that the cooling medium has a significant impact the experimental-analytical correlation.

1. Introduction

Duplex steels have been studied extensively in the past due to the superplastic properties that they exhibit in certain temperature and stress regimes. Due to their microstructural characteristics, these steels offer better corrosion resistance than fully austenitic steels [6] and have increased wear characteristics [8].

Duplex steels, owing to their lower than fully austenitic Ni content, are insensitive to stress corrosion cracking in the majority of chloride reagents, since the ferrite arrests cracks propagating through the austenite while exerting an electrochemical protective effect on the austenite.

One of the most important properties of these steels is their relatively high yield strength [4]. In addition, compared with the austenitic steels, there is little loss of ductility, and therefore, these steels can be drawn with nearly the same ease. Castings made from duplex steels are outstanding for their soundness and cleanness. They can be welded with much less risk of cracking than the fully austenitic grades. If the composition of the electrode is adjusted so that, the weld metal will normally have a duplex structure under weld cooling conditions cracking trouble can be avoided. Nitrogen usually present in these steels, owing to its high diffusivity, aids fast transformation of the weld metal, which solidifies as α to α - γ structure.

The properties mentioned above and the fact that these steels are relatively cheap has made them very attractive for use in pipelines, water pump parts, and agricultural tools. However, although the microstructural parameters of these alloys have been extensively studied [1, 9], it is not well known what the long term changes in their

microstructure are when heat treated. Even though the effect of heat treatment on the mechanical properties of duplex steels is studied in some investigations [5, 7], there is no direct correlation of the materials microstructural characteristics to the employed cooling medium over a wide spectrum of temperatures.

The present work is a metallographic investigation of an SAF2205 alloy (22Cr, 5.5Ni, 3Mo, 0.14N, 0.03C, and 1.7Mn) to experimentally determine its austenite-ferrite equilibria, and correlate the results to the theoretical predictions based on phase diagrams.

2. Experimental Methodology and Set-up

Heat treatment was carried out in an argon direct-quench furnace (Figure 1) in the temperature range 500°C to 1300°C for varying aging times. Aging was followed mainly by direct water quenching to room temperature, while iced brine was used as the quenching medium to study the effect of quenching rate on the microstructure.
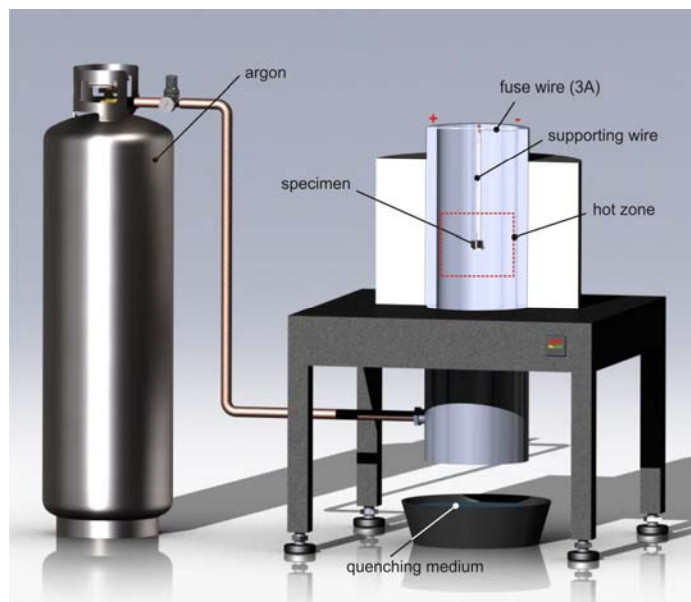

Figure 1. Argon direct-quench furnace.

The material was received in rod form, 15mm in diameter. The rod had been prepared by cold work, annealing at 1050°C and water quenching. A picture, of the as received material, taken by transverse microscopy is shown in Figure 2.
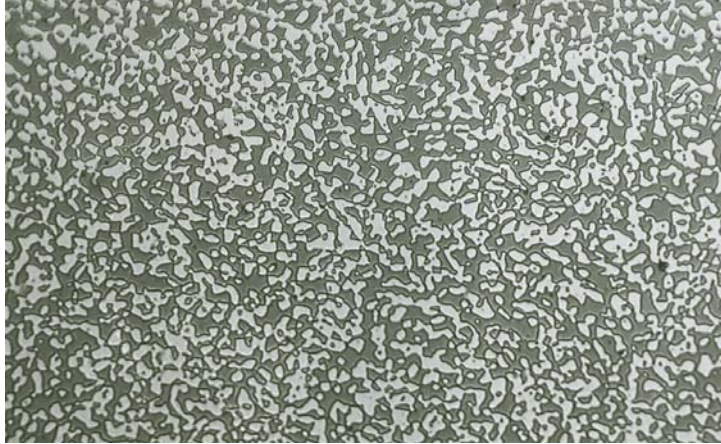

Figure 2. As received material at ×480 magnification.

The rod was cut into small cylinders 8mm in height and 15mm in diameter for use in various experiments. The heat treated cylinders were cut into two symmetric pieces, as illustrated in Figure 3. One was used for optical microscopy and the other for scanning electron microscopy and microanalysis.
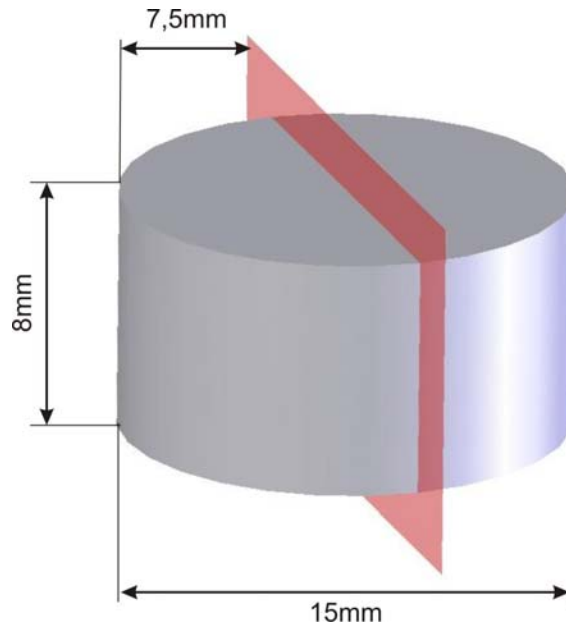
Figure 3. Heat treated cylinders and preparation of specimens.

Specimens for optical and electron microscopy were polished mechanically to 1μm finish. The results presented further on, refer to an average obtained from the measurements Weibull distribution. Etching was done by one of the following methods, depending on the aging temperature.

2.1. Specimens aged below 700°C and between 1000-1200°C

Those intended for optical microscopy were electrolytically etched using 40% KOH at 5V for 15 seconds with the specimen as the anode. This coloured the ferrite grains dark (blue, brown or yellow depending on their distance from the contact point of the electrode) and left unaffected the austenite.

Specimens for electron microscopy were electrolytically etched using 40% KOH at 25V for 10 seconds. This darkened the ferrite and caused surface electrolytic cracks to appear in the ferrite grains, once again leaving the austenite unaffected. These electrolytic cracks were used as a means to distinguish the two phases.

10% oxalic acid electrolytically etched at l0V for 10 seconds was also used to reveal the interphase boundaries and the annealing twins in austenite.

2.2. Specimens aged at 700-1000°C

The heat treated cylinders were etched electrolytically with 40% KOH at 3V for 3 seconds. This did not affect the austenite, while colouring the ferrite dark and revealed a third phase that etched black, thus referred to as "brown phase", demonstrated in Figure 4. Longer etching times or higher voltages result in the third phase being completely dissolved.

10% oxalic acid electrolytically etched at 5V for 10 seconds was also used. This darkened the third phase and left α and γ unaffected. The contrast obtained with this etch, however, was not suitable for scanning microscopy.

2.3. Specimens etched at 1200-1300°C

All samples were immersed into hot water and etched by using Villela's reagent for 2min. The composition of Villela's reagent used was: 5ml HCl, 1gr Picric acid (2,4,6-trinitrophenol), 100ml ethanol (95~), 20g Cr_2O_3, 4.5g NH_4Cl, 18ml HNO_3, 15ml H_2SO_4 plus H_2O to make 1/2 liter.

This darkened the ferrite and slightly affected the austenite. When a few extra drops of concentrated HCl were added, the annealing twins in austenite were revealed.

The microstructures were examined optically at magnifications up to ×600 and photographed by using an Olympus microscope with a 35mm camera. The surface fractions of austenite and ferrite in the two phase specimens were determined directly by using a Quantimet image analysing computer and by point counting. The second was preferred since the error with it was found to be only 5%, whereas with the Quantimet as high as ~20%.

In the three phase specimens, the volume fractions of the phases were determined by using point counting for at least 1000 points.

Scanning electron microscopy and EDAX microanalysis was carried out to study the microstructure and analyse the various phases present.
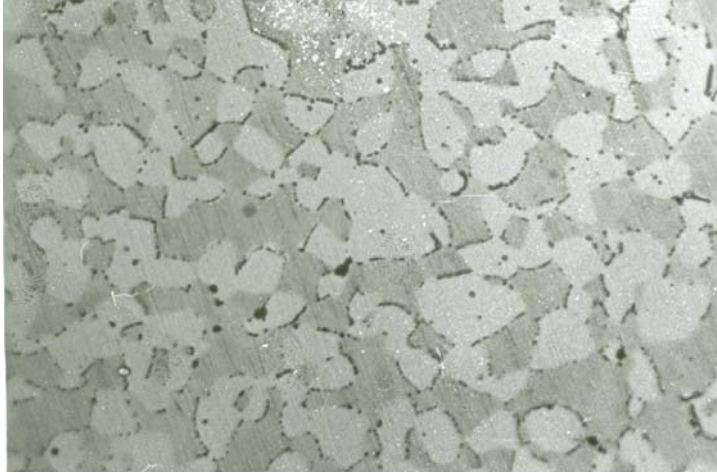
Figure 4. α, γ, and σ at ×520 magnification.

3. Experimental Results

The microstructure of the as-received material consisted of austenite grains in a matrix of ferrite. Figure 2 shows the slightly distorted polygonal austenite grains in the transverse direction after electropolishing in 40% KOH solution at 5V for 10 seconds. Point counting revealed 47.5% ferrite and 52.5% austenite, respectively.

All following experiments were conducted for 4 hours aging of the corresponding specimens. This time frame was chosen to ensure stabilization of the structure even though duplex steels become stable after a few minutes at temperatures above 500°C. Indicial experiments at 1300°C with holding times of 1 hour revealed a transition in the austenite percentage of the specimen when examining areas closer to the surface revealing the effect of holding time, which nevertheless, is very low compared to other materials [10].

In this experiment, a progressively increasing γ% was observed towards the centre of the specimen until after a distance of 6mm, a more or less constant value was reached. Figure 5 shows the increase in austenite % with increasing distance from the surface. This experiment

indicated that aging time has a dramatic effect on the microstructure at these high aging temperatures, and thus a higher holding time was chosen and kept through all experiments to ensure comparability of all treatment temperatures.
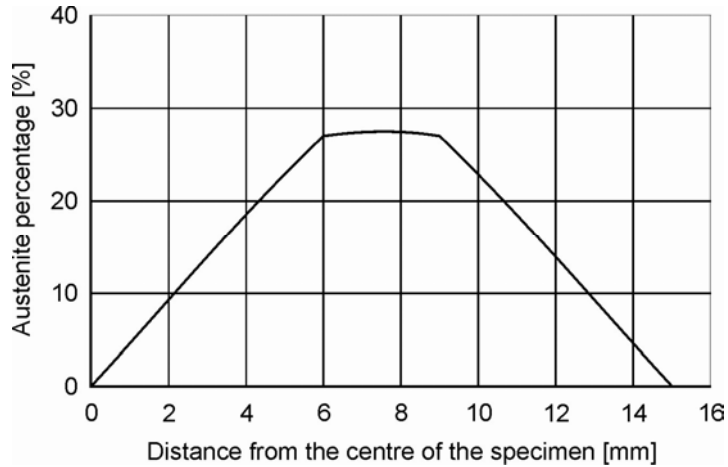

Figure 5. Increase in austenite percentage versus the distance from the centre of the specimen.

This behaviour was attributed to nitrogen loss at high aging temperatures near the surface and since nitrogen, along to other materials as Mn, is an austenite stabilizer these results in smaller amounts of γ phase [3]. A further reason is the lower cooling rate of the specimens centre compared to the outer surface, thus leading to remaining austenite near the center of the specimens. During close examination, this theory was supported by the existence of grain boundary and Widmanstatten austenite.

Aging the as-received material was followed by water quenching to room temperature. During thermal treatment at temperatures higher than 1000°C or lower than 600°C, the two phase α-γ structure was retained, but the relative amounts of the phases changed, while aging in the temperature range 600°C-1000°C, however, resulted in the precipitation of a third phase.

The fluctuation of the experimental results concerning the austenite percentage over the examined temperature range, can be seen in Figure 6, in direct comparison to the analytically determined values [2] based on the thermodynamic data.
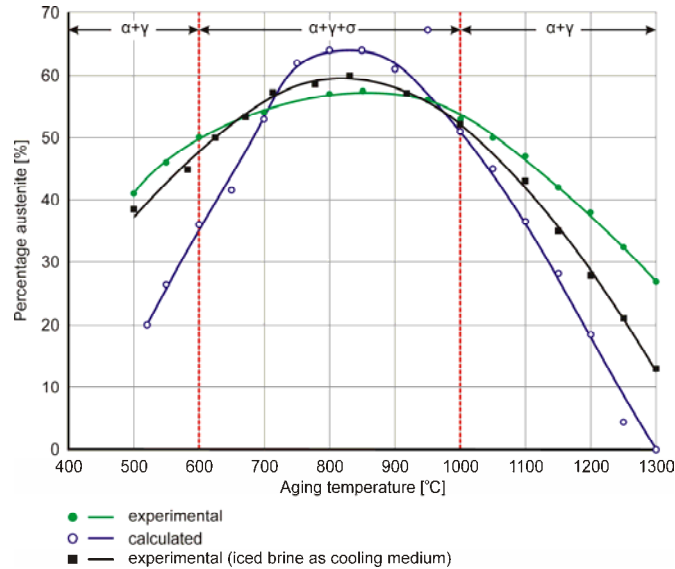

Figure 6. Correlation of calculated and experimentally obtained austenite percentage at the centre of the examined specimens versus aging time.

3.1. Aging in the two phase range

Aging at temperatures higher than 1000°C resulted in an increase of the volume fraction of ferrite at the expense of austenite (as the temperature aggravates). Conversely, aging at temperatures below 600°C, decreased the percentage ferrite in the alloy as the treatment temperature elevated. The temperature 600°C lies on the boundary of the two phase region. Very small precipitates were seen in ferrite grains and on grain boundaries, but their nature could not be determined, due to their small size and volume fraction, by either scanning microscopy or X-ray diffraction.

3.2. Aging in the temperature range

On aging at temperatures between 600°C and 1000°C followed by water quenching the amount of austenite progressively increased at the expense of ferrite until at 850°C, a maximum of 64.6% (surface fraction) was reached. The calculated maximum is 64% and occurs at 825°C. Past this temperature, the amount of austenite decreased in favour of ferrite.

In this temperature range, the precipitation of a third phase, etched brown by 40% KOH, was observed. Figure 4 shows a small number of precipitates (point counting revealed 45.6% α, 54% γ, and 0.4% σ, respectively) at 950°C, which is the highest temperature at which this phase was observed. It appears as spherical or elongated particles on α-γ boundaries that grow in size at the expense of ferrite as the aging time at a particular temperature is increased. The growth of the "brown" phase, however, seems to have no effect on the amount of austenite in the microstructure.

4. Conclusion

The course of the experimental and calculated austenite percentage shown in Figure 6, is contiguous revealing the same tendency of austenite formation and dissolvent during temperature increase. Nevertheless, the deviations of the experimentally-calculated values are considerable, transcending in some cases 20% of the total structure. A closer look at the diagram reveals some interesting tendencies, which could partially explain this phenomenon.

The experiments conducted by using iced brine as quenching medium exhibit a closer collation to the theoretic calculations. This can be attributed to the fact that the thermodynamic model presumes a direct transition of the structure during aging and quenching, which cannot be facilitated experimentally. The usage, however, of iced brine as quenching medium approximates this model far more accurate than direct water quenching, hence presenting better association to the theoretic values.

Bearing this in mind, experimental values approach the calculated ones in an improved way, yet presenting some variations. This may be due to the fact that the calculated data arise from phase diagrams, which are calculated as the austenite fraction in terms of volume, while microstructure analyses are conducted on surfaces and consider only two dimensions. Based on this hypothesis of a third dimension, the relation between austenite volume fraction and austenite surface fraction would not be linear but geometry dependent, which could explain the non-linear deviation of experimental and theoretical values.

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