Study of Sigma Phase in Duplex SAF 2507

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Abstract. Super duplex stainless steel is one of the stainless steel which has a combination between high strength properties and excellent corrosion resistance. However, the resistance can decrease by precipitation of sigma phase which is formed at high temperature, for example after welding processes. A series of experiments has been performed to study the effect of solution annealing to existence of sigma phase on super duplex SAF 2507. Variations of solution-annealing temperatures were 1000 °C, 1065 °C and 1125 °C with holding time of 15 and 30 minutes for each temperature. Effect of solution annealing process was characterized by using XRD, SEM, and Optical Microscopy. The result showed precipitation of sigma phase completely dissolved at 1065 °C and 1125 °C because it reformed to austenite. After it was heated at 1065 °C, chromium carbide appeared in ferrite site and grain boundary. The amount of chromium carbide increased with the increasing of solution annealing temperature.

Keywords: Super duplex, annealing, sigma phase, SAF 2507

1. Introduction

Super duplex stainless steel SAF 2507 is an austenitic-ferritic stainless steel containing 25% Cr and 7% Ni [1]. This material is used for service in highly corrosive condition and high temperature environment due to its excellent corrosion resistance as the result of solution annealing treatment at 1025 °C-1125 °C on the manufacturing process. Sandvik SAF 2507 also has good mechanical properties and impact strength with brittle-ductile transition temperature is below -50 °C (-58 °F). Sandvik SAF 2507 is a duplex stainless steel that specially designed for service in aggressive chloride-containing environments [2]. However, the excellence of mechanical properties and corrosion resistance of SAF 2507 decrease significantly due to the existence of sigma phase.

Sigma phase (σ) is an intermetallic phase with tetragonal crystal structure which is formed at high temperature (320 °C to 955 °C) after holding at a certain period. Sigma phase precipitation occurs when ferrite transforms to secondary austenite and sigma phase (α → σ + γ₂). Precipitation takes place at ferrite sites with rich chromium content of the ferritic stainless steel, grain boundary between austenite and ferrite of duplex stainless steel, and austenite grain boundary of austenitic stainless steel [3]. Sigma phase precipitates at a ferrite grain site because ferrite contains high concentration of chromium, where chromium is known as ferrite former and stabilizer. Nucleation of sigma phase initiates at grain boundary and grows to ferrite grain until transformation ends. Figure 1 shows a correlation between sigma phase formation and energy at the grain boundary. According to [4], when steel is heated to 800 °C-900 °C internal energy of super duplex stainless steel increased. Furthermore,
energy is used by atom for transformation process. Elements of ferrite formers will form ferrite phase, while austenite formers will form austenite phase. Because chromium elements is also a phase stabilizer, then the chromium moves and remains on the center of the grain, hence grain boundary is a site with high energy. When the system search for equilibrium, chromium is attracted to grain boundary and forms sigma phase.

The purpose of this research was to recover corrosion resistance of SAF 2507 by dissolving sigma phase through solution treatment and followed by quenching. The solution annealing temperature to dissolve sigma phase was 1025 °C-1125 °C. In this research SAF 2507 was the solution annealed and followed by water quenching to dissolve sigma phase precipitation to recover the material. The solution annealing temperatures were 1000 °C, 1065 °C and 1125 °C with holding time of 15 and 30 minutes for each temperature.

2. Experimental Method
The test specimen is a seamless tube of super duplex SAF 2507 with a chemical composition as following in Table 1. Specimens are divided into two, namely the control specimen that had sigma phase and heat treatment specimen. The heat treatment performed is solution annealing followed by cooling water quench. Based on ASTM A923[5], the intermetallic phase is formed when the material is exposed to heat at a temperature of 320 °C – 955 °C. To dissolve sigma phase, the specimens is heated at a temperature of solution annealing, held for some time and then water quenching is performed. Temperature variations used were 1000 °C, 1065 °C and 1125 °C. Meanwhile, the variations of holding time used for each temperature were 15 minutes and 30 minutes.

To analyze the microstructure changes of super duplex SAF 2507, XRD, SEM Image-J and OM were conducted. X-Ray Diffraction (XRD) was performed to observe phases, its compound on each sample. Furthermore, XRD was used to investigate the existence of sigma phase as the result of solution annealing. The purpose of Scanning Electron Microscope (SEM) is to observe the morphology of SAF 2507 samples. The optical microscope (OM) was used for microstructure observation of SAF 2507 with different treatment.

| Table 1. Chemical composition of super duplex SAF 2507 [2] |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| C               | Si              | Mn              | P               | S               | Cr              | Ni              | Mo              | Others          |
| ≤0.03           | ≤0.8            | ≤1.2            | ≤0.025          | ≤0.015          | 25              | 7               | 4               | N=0.3           |

Figure 1. Schematization of sigma phase formation in isothermal condition [3]
3. Results and Discussion

3.1. X-Ray Diffraction Test

X-ray diffraction has been carried out with an angle range of 10-100° and wavelength Cu-Kα of 1.54060 Å. XRD generate peaks with certain intensity, and peaks which has high intensity were matched with PDF card to obtain the phases or compounds contained in the sample.

Figure 2 shows the graphic XRD of aging SAF 2507. The result is match with PDF card 47-1417 which shows austenite, PDF card 03-065-9117 which shows sigma phase and also PDF card 85-1410 which shows ferrite phase. This result is confirmed by Ternary diagram of Fe-Cr-Ni in alloying 25%Cr-7%Ni which found sigma phase at a temperature of 1120 K.

XRD of solution annealed samples with holding time of 15 and 30 minutes are shown in Figure 3. Analysis by using PDF card yields phases formed at 1000 °C was austenite, ferrite and sigma. At 1065 °C the austenite and ferrite phases were formed. Meanwhile, at 1125 °C, austenite, ferrite, iron oxide and chromium oxide phases were formed. Sigma phase at heating temperature 1000 °C still existed.
because it incomplete dissolved, while iron oxide and chromium oxide were found at temperature of 1125 °C due to the high temperature oxidation. The decreasing of sigma phase is supported by metallography, SEM, and phase calculation by using image-J.

3.2. Metallography Test
Metallography testing initially was performed to analyze the effect of temperature and holding time of solution annealing to the existence of sigma phase in sample aging of Super Duplex SAF 2507. Observation result is shown in figure 4. The phase formed wereγ-austenite α-ferrite, and σ-sigma. This result is in accordance with a research of [7], which stated austenite phase formed like island, ferrite phase color in black and sigma phase is light colored area surrounding austenite.

Figure 5 shows microstructure of SAF 2507 after solution annealing and holding time of 15 minutes, at 1000 °C, 1065 °C, and 1125 °C. Figure 6 shows microstructure of SAF 2507 after solution annealing and holding time of 30 minutes, at 1000°C, 1065 °C, and 1125 °C. After heating to 1000°C and holding for 15 minutes, microstructures found on SAF 2507 were γ-austenite α-ferrite, and σ-sigma. Sigma phase was still found because it had not dissolved completely. According to ASTM A-480 [6], the minimum temperature of solution annealing was 1025°C. Figure 5b and 5c show the absence of sigma phase. This case is also in accordance to ternary diagram of Fe-Cr-Ni which shows two phase only, austenite and ferrite. Agreed with [3], the metallography result showing the solubility of sigma phase is accordance with growth of ferrite area. The reduction of ferrite area was caused by sigma phase consumes Cr and Mo in ferrite. Besides, as a ferrite former and stabilizer, Cr and Mo are also recognized as a sigma phase former. Due to this characteristic, sigma phase precipitate is in area containing high Cr and Mo.

3.3. Scanning Electron Microscopy Test
Figure 7 is SEM result of an aging sample of SAF 2507. This figure shows austenite phase (island form), ferrite phase (dark area), and sigma phase (boundary region). Ferrite grain size is narrowed due to sigma precipitation which consumes Cr and Mo in ferrite.

Figure 8 is SEM image of the solution annealing with holding time of 15 minutes at 1000°C, 1065°C and 1125°C. While Figure 9 is SEM image of sample of the solution annealing with holding time of 30 minutes at 1000°C, 1065°C and 1125°C. According to Figure 8a, holding time at 1000°C for 15 minutes still left sigma phase due to incomplete dissolution. At temperatures of 1065°C and 1125 °C (Figure 8b and 8c), the sigma phase already vanishes. Phase formed were austenite and ferrite, and carbide found as well on the sample. Number of carbide found at 1125 °C was higher compared to sample at 1065 °C. This is in accordance to research conducted by [8], which stated that chromium carbide precipitates at high temperatures in the ferrite zone because the ferrite forming elements such as chromium is able to diffuse more than austenite. Carbide was formed right after completion of holding time process, where there was a small time interval before quenching occurred.

Table 2 is the result of the calculation of sigma phase in the SEM sample by using image-J software. Sample with aging of SAF 2507 showed number of sigma phase of 34.364%. Sample with solution annealing at temperature of 1000 °C yields number of sigma phase of 26.937% and 26.077% for holding time of 15 minutes and 30 minutes respectively. Based on the calculation phase above, sigma phase tends to decrease and dissolve after solution annealing process. At temperature of 1000 °C, sigma phase decreased with an increasing of holding time.
Figure 4. Microstructure of aging SAF 2507 with 500× magnification

Figure 5. Microstructure of solution annealing SAF 2507, holding time 15 minutes at (a) 1000 °C (b) 1065 °C and (c) 1125 °C

Figure 6. Microstructure of solution annealing SAF 2507, holding time 30 minutes at (a) 1000 °C (b) 1065 °C and (c) 1125 °C

Table 2. Calculation of phase percentage

| Sample       | Austenite (%) + Ferrite (%) | Sigma (%) |
|--------------|-------------------------------|-----------|
| Aging        | 65.636                        | 34.364    |
| SA 1000 – 15 | 73.063                        | 26.937    |
| SA 1000 – 30 | 73.923                        | 26.077    |
| SA 1065 – 15 | -                             | -         |
| SA 1065 – 30 | -                             | -         |
| SA 1125 – 15 | 100                           | -         |
| SA 1125 – 30 | -                             | -         |
4. Conclusion

The effects of solution annealed on precipitation of sigma phase were investigated. Aged SAF 2507 which contains sigma phase remained to exist after it annealed at temperature of 1000°C. While, sigma phase which existed on aged SAF 2507 vanished after solution annealing at temperature of 1065°C and 1125°C. The austenite and ferrite phases exist. Moreover, carbide also was discovered on entire samples.
5. References

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