Influence of the phase balance and cooling conditions on the microstructure and corrosion behavior of solution-treated 1.4462 duplex stainless steel

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Abstract
In this study, effect of cooling rate on the microstructure and corrosion behavior of the solution-treated 1.4462 alloy was investigated. 1.4462 alloy was heat-treated at 1000 °C, 1120 °C and 1200 °C for different duration in order to obtain various phase balance. Two different cooling regimes (rapid cooling and steady cooling) were applied following the solution treatment processes. Also, effect of sigma phase was investigated together with ferrite and austenite phases for steady cooled samples. After heat treatment processes, samples were characterized by an optical microscope (OM), image analysis and scanning electron microscope (SEM). Moreover, hardness tests and electrochemical corrosion tests were applied. According to results, Ferrite ratio and ferrite grain size were increasing with increasing solution treatment temperature and time. Also, ferrite phase was more dominant compared to sigma phase for hardness of the solution-treated samples. Moreover, existing of sigma in higher amount promoted the observation of Epit value.

1. Introduction
Duplex stainless steels (DSSs) have remarkable corrosion resistance and mechanical properties due to existing of ferrite and austenite phases in the microstructure. Ferrite enhances the mechanical strength and pitting corrosion resistance, and austenite enhances the ductility and general corrosion resistance of the DSSs. Higher corrosion resistance and mechanical properties widen the application of the DSSs in the shipbuilding, marine, petrochemical and nuclear industries [1–9].

Microstructure properties of the DSSs exhibit important role in the emergence of desired corrosion resistance and mechanical properties. DSSs are prone to formation of secondary phases at high temperature applications. Intermetallic based secondary phases like sigma and chi occur between 650 °C and 950 °C temperature range. Also, ferrite/austenite phase ratio and grain size can affect the formation of secondary phases. In addition, variation of ferrite/austenite phase ratio and existing of secondary phases in the microstructure affect the corrosion resistance and mechanical properties of the DSSs. Thus, parameters of the solution treatment process such as the cooling condition, holding temperature and duration are very important to obtain desired properties [10–18]. As already mentioned, the pitting corrosion resistance of the DSSs is the outstanding feature of the DSSs. Pitting resistance of the DSSs can be defined by PREN and the PREN is expressed with equation (1) [19]:

\[ \text{PREN} = (\text{Cr wt\%}) + 3.3\times(\text{Mo wt\%}) + 16\times(\text{N wt\%}) \]  

Previous studies have focused on the effect solution treatment temperature on the pitting resistance of the DSSs. Ha et al [20] investigated the relationship between ferrite fraction and pitting resistance of the 1.4462 DSS. Various solution treatment parameters were applied to obtain different phase fraction and ferrite ratio was
ranged from 44% to 63% by annealing at 1050 °C–1195 °C. It was observed that pitting resistance of the sample containing 63% ferrite decreases significantly compared to other samples. Guo et al [21] studied on the effect of annealing temperature on the corrosion behavior of SAF2507 super DSS. Annealing was applied between 1050 °C–1150 °C temperature range and it was determined that volume fraction of the austenite decreases with increasing process temperature. Moreover, Volta potential values of the ferrite and austenite phases were measured and the results were conducted with the corrosion resistance of the samples. It was exhibited that preferential corrosion occurs in the ferrite phase for solution-treated samples and noble volta potential values indicates the higher corrosion resistance. Tan et al [22] also studied the corrosion behavior of annealed SAF2507 alloy. It was revealed that pitting corrosion resistance of the DSS is strongly related with the annealing temperature and it can be determined by the PREN of weaker phase.

In the literature, studies about the effect cooling conditions following the solution treatment are limited. This work studied the influence of the phase balance and cooling conditions on the corrosion behavior of 1.4462 DSS. Samples were solution–treated at various temperature and duration for obtaining different phase fraction. Solution treated samples were water quenched or cooled in the oven with 2 °C min⁻¹ cooling rate. Rapid cooling (quenching) provided the protection of ferrite and austenite fraction obtained during the solution treatment process. Also, steady cooling (cooling in the oven with 2 °C min⁻¹) resulted in formation of secondary phases together with ferrite and austenite and various phase fractions were obtained by annealing. Solution treatment parameters were given in table 2.

All samples were grinded with SiC emeries from 180 mesh to 2000 mesh and polished with 1 μm diamond paste. The electrolytic etching was applied in 5% KOH solution with 3.0 V for 5 s to reveal microstructures. All metallographic examinations were performed from cross-sectional areas to obtain accurate microstructure properties.

Microstructural characterization of the samples was performed by optical microscope (OM) (Nikon Eclipse MA 100), scanning electron microscope (SEM) (Zeiss EVO LS10) and image analysis. Also, hardness of the samples was investigated by Vickers hardness test with HV₀.3.

### 2. Experimental

1.4462 DSS was used in experimental studies and chemical composition of the alloy was given in table 1.

Solution treatments were applied to 1.4462 DSS samples for obtaining various ferrite and austenite phase fraction. Solution treated samples were water quenched or cooled in the oven with 2 °C min⁻¹ cooling rate. Rapid cooling (quenching) provided the protection of ferrite and austenite fraction obtained during the solution treatment process. Also, steady cooling (cooling in the oven with 2 °C min⁻¹) resulted in formation of secondary phases together with ferrite and austenite and various phase fractions were obtained by annealing. Solution treatment parameters were given in table 2.

### Table 1. Chemical composition of the 1.4462 DSS (wt%).

|   | C  | Si | Mn | Cr  | Mo | Cu |
|---|----|----|----|-----|----|----|
| Ni | 0.019 | 0.50 | 1.46 | 22.70 | 3.19 | 0.50 |
| Ni | 0.047 | 0.030 | 0.0001 | 0.156 | Bal. |

### Table 2. Solution treatment parameters.

| Sample Name | Solution Treatment Temperature (°C) | Solution Treatment Time (minutes) | Cooling Condition |
|-------------|------------------------------------|----------------------------------|-------------------|
| S1          | 1000                               | 30                               | Rapid cooling     |
| S2          | 1120                               | 30                               | Steady cooling    |
| S3          | 1200                               | 480                              | Rapid cooling     |
| S4          |                                    |                                  | Steady cooling    |
| S5          |                                    |                                  | Rapid cooling     |
| S6          |                                    |                                  | Steady cooling    |
Corrosion properties of the samples were determined by potentiodynamic polarization tests. Potentiodynamic polarization test was performed with triple electrode system and that system consisted of working electrode (samples), a reference electrode (Ag/AgCl) and a counter electrode (platinum). The surface area of the working and counter electrodes were settled as 1 cm² and 4 cm², respectively.

3. Results and discussion

Microstructure of the commercial 1.4462 DSS can be seen in figure 1. Grey phase indicates the ferrite (δ) and also light phase indicates the austenite (γ). DSSs solidify as ferrite and austenite forms beside ferrite at lower temperatures.

Microstructures of the heat-treated samples can be seen in figure 2. Grey phase indicates the ferrite (δ) and light phase indicates the austenite (γ). Moreover for the steady cooled samples, dark phase indicates the sigma phase (σ). Generally, DSSs consist of dual phase structure. During the solidification of the alloy, ferrite nucleates from liquid metal and austenite forms at lower temperatures. Also, solution treatment process can be applied in order to obtain equal amount of ferrite-austenite phase ratio and ferrite phase ratio can exceed the 50% for enhanced heat treatment temperature and time. Another important factor for the solution treatment process is the cooling regime following holding section. Higher cooling rates can provide the protection of obtained ferrite-austenite phase balance for room temperature. However, steady cooling regimes cause the formation of intermetallic phases at 900–600 °C temperature range via diffusion based nucleation and growth mechanism. As seen in figures 2(a)–(c), intermetallic based sigma phase occurred at ferrite-austenite and ferrite-ferrite grain boundaries. Sigma phase is a chromium rich and thus, it grew into chromium rich ferrite following the nucleation at grain boundaries.

Figure 3 shows the SEM images of steady cooled samples. Figure 3 clearly indicates that ferrite-ferrite grain boundary is preferred nucleation site for the sigma phase. DSSs include chromium and nickel as the main alloying elements.

Chromium is a ferrite stabilizer, while nickel is an austenite stabilizer. Thus, chromium content of the ferrite is higher than the austenite. It is mentioned earlier that sigma is a chromium rich intermetallic phase and chromium is essential for the nucleation and growth of the sigma phase. During the steady cooling of solution-treated samples, diffusion was dominant and sigma phase occurred at ferrite-ferrite grain boundaries via chromium diffusion from ferrite grain interiors to boundaries. Moreover sigma phase grew into ferrite phase and ferrite phase ratio was decreased due to formation of sigma.
As mentioned earlier in order to obtain different microstructure properties and phase proportions, commercial 1.4462 DSS was heat-treated with various process temperature and time. Resultant phase ratios can be seen in figure 4. Rapid cooled samples were consisted of ferrite and austenite phases. Also, ferrite ratio was increased with increasing solution treatment temperature and time. Ferrite phase ratio and ferrite grain size increase at higher process temperature and time. Thus, sample solution treated at 1200 °C for 480 min and rapid cooled had the highest ferrite ratio. Moreover, steady cooled samples were consisted of ferrite, austenite and sigma phases. Steady cooling condition revealed lower cooling rates and sigma phase occurred at 900–600 °C temperature range during the cooling of solution-treated samples. The highest sigma phase ratio was obtained for the lowest solution treatment temperature and time. Sigma phase can form by the eutectoid decomposition of the ferrite. The ratio and stability of the ferrite phase were increased with enhanced solution treatment temperature and time, and thus eutectic decomposition of the ferrite became difficult during the steady cooling of the samples. Also, austenite ratio was increased for the steady cooling condition due to decomposition of ferrite into sigma and austenite. At lower solution treatment temperature and time, formation of sigma phase was dominant and reformation of austenite occurred at lower rates. However at higher solution treatment temperature and time, ferrite phase became more stable and during the steady cooling, reformation of austenite occurred at higher rates, while the formation of sigma was obtained at the lowest rate.

Ferrite/ferrite and ferrite/austenite grain boundaries were observed for each sample (figure 5) and Ferrite grain boundary lengths of the solution-treated samples were given in figure 6. Ferrite grain boundary length decreased with increasing heat treatment temperature and time. It has been emphasized that ratio and stability of the ferrite phase increase with enhanced process temperature and time. Moreover it was clearly deduced from the figure 6 that grain boundary length of the ferrite phase is dramatically decreasing with increasing process.
temperature for rapid cooled sample. Decreases in ferrite grain boundary length mean that nucleation sites for sigma formation are reduced. Therefore, sigma phase ratio decreased with increasing heat treatment temperature and time for steady cooled samples. Furthermore, the ferrite content decreased with increasing heat treatment temperature and time for the steady cooled samples. The larger grain size of the initial ferrite phase also reduced the ferrite grain boundary length in the steady cooled samples and resulted in the formation of a larger grain ferrite phase.

Hardness values of the solution-treated samples were given in figure 7. The main parameters that determine the hardness values of the samples were the ferrite-austenite phase balance and the sigma phase ratio. As the ferrite content of the rapid cooled samples, the hardness value increased. In steady cooled samples, the sigma

Figure 3. SEM images of the steady cooled samples.
phase ratio did not significantly increase the hardness. The highest hardness for the steady cooled samples was obtained in the sample 4, where ferrite and sigma phases were in a balanced ratio. In addition, it was found that the hardness value for solution conditions is more dependent on ferrite phase properties than sigma phase. The highest hardness value was obtained in sample 5 which did not contain sigma phase but had the highest ferrite content.

Figure 4. Phase ratios of the samples after the applied solution treatment processes.

Figure 5. Representative microstructure of the DSS for the grain boundary measurements.
Higher $E_{corr}$ value delays the formation of corrosion damage in the corrosive media. On the other hand, high $i_{corr}$ value indicates that corrosion damage will progress rapidly and the corrosion rate of the material will be high in particular corrosive environment. The greatest $E_{corr}$ value was obtained for sample 2 that contains the highest sigma phase ratio. Occurrence of corrosion damage was going to initiate later for sample 2 compared to other samples. The main reason of this result was the formation of secondary austenite during the precipitation of sigma with the eutectoid decomposition of ferrite. Increased austenite ratio increased the general corrosion
resistance. However, sample exhibited active dissolution behavior with the occurrence of corrosion. In addition, pitting corrosion of the material was observed with the formation of sigma phase and a significant Epit value was obtained as shown in the figure 8. However, the sample with the highest ferrite content also had a high icorr value. It was related with lower corrosion resistance of the ferrite compared to austenite.

4. Conclusion

- In this study, the effect of the cooling conditions on the microstructure and corrosion properties of the solution-treated 1.4462 alloy was investigated.
- With increasing solution treatment temperature and time, the ferrite content of the alloy was increasing, while the ferrite grain boundary length was decreasing.
- The ferrite grain boundary is very important for sigma phase formation. As the ferrite grain grew and the ferrite grain boundary decreased, the ratio of the sigma phase occurred in steady cooled samples decreased.
- Ferrite phase is more effective on hardness than sigma phase.
- The higher amount of sigma phase promoted the pitting and Epit value was observe

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