Research Article

Determination of Susceptibility to Intergranular Corrosion of UNS 31803 Type Duplex Stainless Steel by Electrochemical Reactivation Method

Mehmet Emin Arıkan,¹ Rafet Arıkan,² and Mustafa Doruk¹

¹ Department of Metallurgical & Materials Engineering, METU, 06531 Ankara, Turkey

² Department of Mechanical Engineering, Atılım University, Incek, 06836 Ankara, Turkey

Correspondence should be addressed to Rafet Arıkan, rarikan@atilim.edu.tr

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Specimens taken from a hot-rolled cylindrical duplex stainless steel (DSS) bar with 22% Cr grade were solution annealed at 1050°C and then aged at 725°C from 100 to 31622 min for sensitization treatment. Double loop electrochemical potentiodynamic reactivation and standard weight loss immersion acid tests were conducted. The solution-annealed samples were found unsensitized. Those samples aged for 100 and 316 min were less sensitized whereas samples aged for 1000 min and especially those aged for 3162, 10000, and 31622 min were heavily sensitized. The degree of sensitization (DOS) can be attributed to higher contribution of chromium- and molybdenum-depleted areas resulting from intermetallic phases.

1. Introduction

Generally, duplex stainless steels (DSS) are Fe-Cr-Ni alloys having an approximately volumetric fraction of 50% ferrite and 50% austenite in their microstructures. Their main feature is that they compromise the favorable corrosion resistance of austenitic stainless steels with good mechanical properties [1–4].

In duplex stainless steels undesirable phases such as intermetallic phases (sigma and chi), carbides, and nitrides may exist if the manufacturing processes are not carefully controlled. High levels of elements stabilizing ferrite, such as chromium, molybdenum, and silicon, can promote the formation of sigma phase (σ). Sigma phase (σ) is a hard and brittle intermetallic phase, which is generally formed between 600 and 950°C with rapid formation kinetics [5–7]. Additional phases found in duplex stainless steels can include chi (χ), laves (η), and α' [8]. The nucleation sites for σ and χ phases are grain boundaries, incoherent twin boundaries, and dislocations. Duplex stainless steels are susceptible to sensitization due to the precipitation of additional phases when heated in a temperature range of 600–950°C. These

phases have a reverse effect on the corrosion and mechanical properties [6, 7]. A substantial depletion of Cr and Mo due to a copious precipitation of σ and χ phases results in a decrease of the corrosion properties [9].

There are several test methods for determining the sensitization to intergranular corrosion. Weight loss acid test was first standardized, and the test procedure was presented in ASTM A262-91 [10]. Corrosion rate is determined by measuring the weight loss of the sample. Another test method of measuring the degree of sensitization to intergranular corrosion involves electrochemical reactivation of the steel samples as defined in ASTM G108-94 [11]. This reactivation process is named as electrochemical potentiodynamic reactivation (EPR) and has been developed in single-loop (SLEPR) or in double-loop (DLEPR) types. The latter was first used for austenitic stainless steels. The best advantage of this technique is that it obtains a quantitative value of the degree of sensitization instead of an only qualitative appreciation as metallographic etchings. The EPR test provides the degree of sensitization of the material which is proportional to the amount of chromium-depleted areas adjacent to the Cr-rich phases.

In this study, DLEPR was applied for the determination of susceptibility to sensitization of duplex stainless steel type UNS S31803 with 22% Cr grade. It is designated by X2CrNiMo 22-5-3 with the trade name SAF2205. The summary of technical literature related to austenitic-ferritic duplex stainless steels shows that the test solution for DLEPR often consists of sulphuric acid (H_2SO_4) solution with the addition of KSCN as depassivator.

The purpose of the present work was to investigate intergranular corrosion behavior of DSS in relation to the influence of the microstructure produced by different heat treatments. This is performed by solution annealing and ageing for different times up to 22 days in order to provide different microstructure and sensitization levels. Electrochemical measurements were used to determine the degree of sensitization (DOS) to intergranular corrosion. Light optical microscopy (LOM) was used to identify the different phases that form in bulk material after the heat treatments. X-ray diffraction (XRD) technique and energy dispersive system (EDS) analysis were used for microstructural evolution. Surfaces obtained after the DLEPR test and the weight loss immersion test were also observed to check the attack locations and the relationship with the chromium-depleted areas.

A similar work was performed by Arikan and Doruk [12] on the same type duplex stainless steel aged at 650°C for various periods of time. The results will be compared in Section 3.6.

2. Experimental Method

2.1. Materials and Heat Treatments. The material used in this research was a commercial type hot-rolled bar of UNS S31803 duplex stainless steel (DSS) (trade name SAF2205). The chemical composition of the steel is given in Table 1.

The specimens were cut from a wrought cylindrical bar of 100 mm in diameter and 200 mm in length. The specimens were also in a cylindrical shape of 10 mm in diameter and 20 mm in length. They were taken from the bar in an orientation parallel to the rolling direction. In order to homogenize the structure, all specimens were subjected to a solution heat treatment at 1050°C for 1 hour and then quenched in water, followed by ageing heat treatments at 725°C for various periods of time.

2.2. Metallography. After heat treatments, the surfaces of the specimens were ground from 400 to 2000 grit emery paper. For microstructure examination, the surfaces of the specimens were polished with 9 and $1\mu\text{m}$ diamond paste. For metallographic examination, they were etched in NaOH solution as described in ASTM A923 [13]. It colors the phases in duplex stainless steel such as austenite in white, ferrite in light brown, sigma in dark brown, and carbides in black.

2.3. Weight Loss Test. The weight loss test was done according to ASTM A923-03 Test Method C standard. The test solution was prepared by dissolving 100 g of reagent grade ferric

TABLE 1: Chemical composition of 2205 DSS (wt.%).

C	Cr	Ni	Mo	Mn	Fe
0.026	22.04	4.45	2.69	1.49	Ret.

chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in 900 mL of distilled water (6% FeCl_3 by weight). The pH of the solution was adjusted to approximately 1.3 by addition of HCl or NaOH. The corrosion rate was evaluated as the rate of weight loss in mg per sq·dm per day (mdd).

2.4. X-Ray Diffraction Analysis. The chemical composition and the profile line analysis of the phases were carried out by EDS with SEM. The presence of different phases was also identified by X-ray diffraction patterns by means of Rigaku diffractometer with $\text{Cu } K_\alpha$ radiation.

2.5. DLEPR Tests. The susceptibility of the aged DSS to intergranular corrosion was evaluated using DLEPR test according to ASTM G108 standard [11]. The test was performed according to the recommendations of Majidi and Streicher [14, 15]. The standard solution is modified to suit duplex stainless steels and consisted of 2 M H_2SO_4 + 0.5 M NaCl + 0.01 M KSCN at $30 \pm 1^\circ\text{C}$. The test cell consisted of a 1 litre flask with necks for electrodes. A cylindrical working electrode was centrally located, and two counter electrodes were placed next to specimen to improve the current distribution. The specimen was mounted according to Stern-Makrides arrangement [11].

The potential was scanned with a rate of 15 V/hour in the anodic direction from a potential lower than E_{corr} in the cathodic region to a point of 0.250 V in middle of the passive region. The scanning direction was then reversed, and hence two loops are generated. The peak activation current (I_a) and the peak reactivation current (I_r) were measured during the forward and backward scans, respectively. The degree of sensitization (DOS) was thus measured as the ratio of the maximum current densities, $(I_r/I_a) \times 100$ [14, 15].

The activation or critical current density (I_a) or (I_{crit}) is proportional to the corrosion rate of a metal. The rate of corrosion rises rapidly in the activation range up to the activation peak current density. The potential corresponding to this is called activation peak potential E_a or passivation potential E_{pass} . If the potential is raised further, the anodic current will drop to a lower value called passivation current density (I_{pass}), and then it will remain constant over a wide potential range. This is the passive range in which a thin invisible film of oxide covers the metal surface. This protective film acts as a barrier between the metal and its environment and reduces the rate of dissolution.

During the anodic sweep, the entire surface is active and contributes to the peak current. But during the reactivation sweep, only the sensitized regions contribute to the passive-active transition. The unsensitized specimens show a small I_r and results in a small (I_r/I_a) ratio. On the other hand, in heavily sensitized specimens, I_r approaches I_a resulting in a high (I_r/I_a) ratio.

FIGURE 1: Microstructure of DSS, solution annealed at 1050°C for 1 hour (austenite in white, ferrite in gray).

3. Results and Discussion

3.1. Metallographic Examination. The optical micrographs obtained by etching with NaOH reagent are given in Figures 1 and 2. Figure 1 represents the microstructure of solution-annealed parent alloy in which white phase is austenite (γ) and the dark phase is ferrite (α). The volume fractions of α and γ were 0.54 and 0.46, respectively. The microstructure does not reveal any visible precipitates of other phases.

To study the influence of the microstructure on degree of sensitization (DOS), the specimens were aged at 725°C for times 100, 316, 1000, 3162, 10000 and 31622 min. The ageing heat treatments induced a marked change in the ferrite/austenite ratio caused by the transformation [16]

where γ_2 is the so-called secondary austenite. The nucleation rate [17, 18] and the growth kinetics of this reaction have been studied extensively [19]. It is well known that the controlling step is the nucleation rate. The growth of sigma phase causes a decrease in chromium and molybdenum content of the neighboring ferrite which becomes unstable and transforms into new austenite. This austenite, in turn, is rich in chromium and molybdenum and has a lower content of nickel if compared with the neighboring primary austenite. These changes in chemical composition promote the formation of an additional sigma phase. The overall result is the coprecipitation of secondary austenite and sigma.

For specimens aged at 725°C, microstructural changes are shown in Figures 2(a) and 2(f). For ageing from 100 to 316 min, the first tiny precipitates of sigma phase appear at α/γ and α/α boundaries. Incoherent twin boundaries and dislocations inside the ferrite matrix may also be the nucleation sites for precipitation [20]. The precipitations of σ -phase were first encountered after ageing for 316 min and the size and amount of σ phase increased with ageing time. Nucleation and growth of σ -phase are thermally activated processes involving diffusion. Therefore, temperature will have a significant effect on the kinetics of the transformation. After 1000 min, a lot of sigma precipitates have developed at

α/γ , α/α , and inside the ferrite phase as shown in Figures 2(c) and 2(f). Longer ageing treatment leads to the increase and coarsening of the σ phase in an irregular shape.

3.2. Phase Volume Fraction by Light Optical Microscopy. Microanalysis reveals that the solution-annealed material consists of ferrite and austenite phases. The main microstructural change during ageing is the formation of σ -phase and secondary austenite (γ_2) from the ferrite phase due to the eutectoid reaction ($\alpha \rightarrow \sigma + \gamma_2$). The amounts of phases were estimated by measuring the fractions of colored area on polished and etched specimens by light optical microscopy (LOM). The measured volume fractions of ferrite, austenite, and sigma phases for different ageing times are given in Table 2 and Figure 3. Since the ferrite transforms into σ and γ_2 , the ferrite phase decreases as the volume percentages of sigma and secondary austenite increase with ageing time until the whole ferrite is totally consumed. Ferrite continuously decreases throughout each of the isothermal holds and reaches zero at the end of the 31622 min. The total austenite is considered as the sum of the primary and secondary austenite ($\gamma + \gamma_2$) and increases to the value of 57% by time.

During the early stages of the transformation, sigma forms preferentially at the α/γ and α/α grain boundaries and inside the α -grain and grows into the ferrite phase via a transformation mechanism involving diffusion. Because both nucleation and diffusional growth of σ are thermally activated processes, the ageing time and temperature will have a significant effect on the kinetics of the transformation. The time at which sigma was first observed was 316 min at 725°C.

3.3. Weight Loss Test Results. The degree of sensitization is also given by the loss of weight due to the dissolution of chromium-depleted areas and is expressed as the rate of weight loss in mdd. The results of standard weight loss immersion test are given in Table 3 and plotted in Figure 4. Corrosion rate of the specimens aged at 725°C is low up to 1000 min and then increases rapidly up to 31622 min. Moreover, the lower chromium and molybdenum content is not the only factor responsible for the increase in the rate of corrosion. The neighborhood of more noble phases (sigma phase) will enhance the anodic dissolution of secondary austenite extensively.

The surfaces of the corroded specimens were examined using LOM. The localized attack in black points is initiated in the secondary austenite phase adjacent to the sigma phase as shown in Figure 5. The austenite and the sigma phase resist the ferric chloride solution more than the ferrite and the secondary austenite. Once a pit is formed it rapidly propagates within the initial ferrite region. As a result, it is observed that the sigma and austenite phases are almost intact, while the secondary austenite (γ_2) and some iron rich ferrite phases are attacked.

3.4. EDS Analysis of Phases. The precipitation of the intermetallic sigma phase is accomplished by the formation

FIGURE 2: Optical micrographs obtained after ageing at 725°C by etching with NaOH reagent (a) 100 min, (b) 316 min, (c) 1000 min, (d) 3162 min, (e) 10000 min, (f) 31622 min (austenite in white, ferrite in gray, sigma precipitates in black).

of secondary austenite (γ_2). As the sigma phase grows, chromium and molybdenum are enriched in these precipitates, and, simultaneously, nickel diffuses into the ferrite. The enrichment of γ -stabilizing elements (such as Ni) in the ferrite and the loss of ferrite stabilizing elements (such as Cr and Mo) lead to an unstable ferrite transforming into secondary austenite depleted in chromium and molybdenum [20].

The EDS measurements of Cr, Mo, Ni, Mn, and Fe content of the α , γ , σ , and γ_2 phases present in samples of solution annealed and aged for 31622 min are given in Table 4. During the growth of sigma phase, these elements diffuse from the surrounding ferrite matrix to the sigma phase, and this causes depletion in these elements. The depletion in chromium and molybdenum leads to the transformation of the region to secondary austenite (γ_2).

TABLE 2: The phase volume percentages obtained from digital image analysis.

Heat treatment	Ageing time (min)	Ferrite phase (vol. %)	Austenite phase ($\gamma + \gamma_2$) (vol. %)	Sigma phase (vol. %)
Solution annealed at 1050°C, 1 h		54.55	45.45	0
	100	54	46	0
	316	53.2	46.2	0.6
Solution annealed at 1050°C, 1 hr + aged at 725°C	1000	32	49	19
	3162	15	52	33
	10000	6	54	40
	31622	0	57	43

FIGURE 3: Changes in volume % of austenite, ferrite, and sigma phases with ageing time at 725°C.

TABLE 3: Weight loss immersion acid test results according to ASTM A 923-03.

Ageing time (min)	Weight loss (mdd)
100	0.49451
316	2.37328
1000	5.38945
3162	5.16104
10000	5.28002
31622	6.04718

3.5. X-Ray Diffraction Pattern. The results of the X-ray diffraction analysis consist of a series of diffraction patterns given in Figure 6. The diffraction pattern of the solution-annealed parent alloy presents ferrite and austenite phase peaks only. Samples aged at 725°C for different ageing times show the peaks of phases developed.

Although the precipitations at grain boundaries are evident for 316 min of ageing as shown in light optical micrograph of Figure 2(b), the X-ray spectra of the sample do not reveal any sigma peak. This may be attributed, as given in Table 2, to the very low volume fraction of the sigma phase (0.6%).

Samples aged at 725°C show sigma peaks first in 1000 min of ageing. With increased holding time, the intensity of sigma peaks increases as the volume fraction of sigma phase increases (Table 2), and also additional sigma

FIGURE 4: The change in weight loss with ageing time.

FIGURE 5: Dissolution of the secondary austenite in weight loss test (black: attacked region in the secondary austenite phase adjacent to the sigma phase, gray: austenite, and white: sigma).

peaks appear. After 3162 min of ageing, one of the ferrite phase peaks decreases to nearly zero but the other peak does not disappear; it overlaps with a sigma phase peak. After longer periods of time such as 10000 min, the treatments promote the transformation of ferrite phase. This results in a noticeable decrease in the intensity of the α and an increase of γ peaks. The decrease of the ferrite peak intensity indicates that the major fraction of ferrite is transformed into sigma. Consequently several sigma peaks are observed. All the changes observed in the diffraction peak intensity do correlate well with the changes in volume fraction of each phase during the isothermal hold as given in Table 2.

TABLE 4: EDS analysis of phases present in solution-annealed and aged condition of DSS.

Heat treatment	Phase	Cr (wt. %)	Ni (wt. %)	Mo (wt. %)	Mn (wt. %)	Si (wt. %)	S (wt. %)	Fe (wt. %)
Solutionannealed	General composition	22.04	4.45	2.69	1.49	0.45	0.003	68.29
Solution annealed	α	26.32	4.87	4.15	1.59	0.74	—	62.32
	γ	23.55	7.08	—	1.85	—	1.19	66.33
725°C/31622 min	γ	23.81	6.43	—	—	—	—	69.76
	σ	35.21	—	7.21	—	—	—	57.58
	γ_2	23.03	6.91	—	—	1.04	1.26	67.75
	γ_2	18.65	5.21	—	—	—	—	76.14

FIGURE 6: X-Ray diffraction patterns of samples aged at 725°C.

3.6. DLEPR Results. Figure 7 shows the polarization curves for samples in solution-annealed and aged condition. The curve obtained from the solution-annealed sample is treated as a reference and compared with the others. The activation peak current density of the reference curve is 23.13 mA/cm², and the corresponding activation peak potential (E_a) or passivation potential (E_{pass}) is −212.78 mV with respect to saturated calomel reference electrode (SCE). This peak reaches a maximum and then fall, to a low passive current density (I_{pass}) of 0.001448 mA/cm² before reaching the chosen reverse potential of +250 mV. The sample is thus passivated in a wide range between −212.78 mV and +250 mV. In this passive range, a thin invisible film of oxide may cover the metal surface. The protective film acts as a barrier between the metal and its environment and reduces its rate of dissolution. And hence, the I_r/I_a ratio is very low (0.027634%). This may be considered as unsensitized material (Table 5).

From the samples aged for 100 min, any visible precipitate is not observed either optically (Figure 2(a)), or in XRD analysis (Figure 6). After ageing for 316 min, sigma phase nucleation starts at α/γ phase boundaries as shown in Figure 2(b), but the diffraction pattern (Figure 6) does not reveal any evidence due to very small amount of the sigma phase (0.6%), (Table 2). The samples aged for 100 and 316 min present very small reactivation currents (Table 5), and hence the I_r/I_a ratios are 5.76 and 6.48%, and accordingly the corrosion rates become 0.49451 and 2.37328 mdd,

respectively. This means slight chromium depletion resulting in a less sensitization.

After 1000 min, the σ precipitates have grown at the boundaries and within the ferrite grains. Next to the growing σ -phase, the secondary austenite (γ_2) forms from the decomposition of ferrite into σ and γ_2 (Table 2). Dissolution of the secondary austenite results in greater weight loss (5.38 mdd) (Table 3) and accordingly a high ratio of I_r/I_a (53.42%) (Table 5). This means that the sample has been highly sensitized.

After 3162 min of ageing, a substantial decrease in chromium content of the interfaces and around the precipitates reduces the corrosion resistance and makes the alloy more susceptible to localized attacks. This leads to the highest grade of sensitization, and thus the DOS value reaches 93.189% (Table 5), and dissolution of the secondary austenite (γ_2) results in a corrosion rate of 5.161 mdd (Table 3).

Similar results were obtained for the same reasons after ageing for 10000 and 31622 min. The corresponding DOS are 90.4 and 92.39%, and the mdd values are 5.28 and 6.04 respectively, showing the samples being heavily sensitized (see Table 5 for comparison).

When the polarization curves of the samples aged at 725°C from 100 to 31622 min are compared with the reference curve, it is seen that the activation peak current density increases with increasing ageing times (Table 5). And also the passive current density increases from 0.033688 mA/cm² up to 0.059391 mA/cm², and the passivation potential (E_{pass}) decreases from −212.78 mV to −172.23 mV.

From the results discussed so far considering weight loss acid test and DLEPR test, it can be concluded that both the sensitization and the corrosion rate have increased with respect to the depletion of chromium and molybdenum in the ferrite region.

Chromium diffusion is much faster in ferrite than in austenite. The chromium concentrates in the neighboring sigma phase [21] and causes the sigma phase to grow fast within the ferrite region. As a result, the formation of the secondary austenite can degrade the stability of the passive film [22].

After the DLEPR test, a sample aged for 31622 min was slightly polished and examined with LOM (Figure 8(a)) to check the attack locations and the relationship with the chromium-depleted areas.

Observation of the surface indicates that the sigma and austenite phases are almost intact, while the secondary

FIGURE 7: DLEPR curves plotted for DSS after solution and sensitization heat treatments at 725°C between 100 and 31622 min (scan rate: 15 V/hr).

FIGURE 8: Optical micrographs after DLEPR test for sample aged at 725°C for 31622 min (a) after slightly polished (large austenite in white, attacked regions in black, sigma: small white regions) (b) electrolytically etched with NaOH (austenite in white, sigma in brown, attacked regions in black).

TABLE 5: DLEPR Test results of 2205 type duplex stainless steel.

Temperature (°C)	Time (min)	Activation peak potential, E_a (mV)	Activation peak current density, I_a (mA/cm ²)	Reactivation peak potential, E_r (mV)	Reactivation peak current density, I_r (mA/cm ²)	Passivation current density, I_{pass} (mA/cm ²)	DOS ($I_r/I_a \times 100$)
Solution annealed at 1050°C, 1 hr		-212.78	23.1304849	-267.33	0.0063918	0.001448	0.027634
Solution annealed at 1050°C, 1 hr + aged at 725°C	100	-178.33	29.2261754	-196.13	1.6857088	0.033688	5.767805
	316	-185.25	26.5737074	-189.43	1.7231466	0.037542	6.484404
	1000	-172.22	42.2727750	-177.35	22.5825614	0.052615	53.421053
	3162	-199.68	54.2137581	-195.70	50.5214698	0.062409	93.189389
	10000	-183.47	55.7856777	-191.11	50.4425582	0.057675	90.422059
	31622	-147.94	69.6430296	-160.30	64.3463484	0.059391	92.394528

austenite and some iron rich ferrite phase are attacked. The corroded secondary austenite regions appear in black, and the isolated sigma precipitates in white. Large primary austenite grains remain in white as usual. To distinguish sigma and primary austenite phases in color, the samples were electrolytically etched with NaOH reagent. The sigma phase is colored reddish brown and distinguished from the primary austenite which was not affected from the etchant (Figure 8(b)).

When compared to the acid test samples (Figure 5), the DLEPR specimens showed a similar behavior, because the same areas were affected in both cases. In other words the attacks have occurred at sensitized areas. The appearance of the localized attack after immersion testing shows large number of black points clearly. This shows that local corrosion is initiated in the secondary austenite phase as happened in the DLEPR test samples. Once a pit is formed, it rapidly propagates within the initial ferrite region. After a long time of exposure, the corroded area extended and covered a large area including many sigma and austenite phases. As a result large cavities were developed. This type of corrosion is known as localized corrosion.

As mentioned before, Arikan and Doruk presented a study [12] dealing with DLEPR and standard weight loss acid tests for the same type of duplex stainless steel annealed at 1050°C for 1 hour and aged at 650°C for various periods of time.

Comparison of the results obtained from samples aged at 650 and 725°C indicates that the minimum time where sigma was first observed is less than 316 min at 725°C and longer as 1000 min at 650°C. Both DLEPR and acid tests expose continuous chromium-depleted zones leading to intergranular corrosion at α/γ phase boundaries and local corrosion around sigma phases precipitated inside the ferrite region.

Corrosion rate of samples aged at 650°C is very low up to 1000 min and then increases up to 31622 min, whereas the rate for samples aged at 725°C is very low only for 100 min of ageing and then rapidly increases with ageing time (Table 3).

A similar trend for DOS values was observed at 650 and 725°C, but since ferrite decomposition occurs faster at 725°C, accordingly sensitization begins in shorter time of ageing than that at 650°C. This indicates that The DLEPR test provides results proportional to σ -phase content.

As a result, in both cases, the sensitization and corrosion rate depend strongly on the extent of chromium and molybdenum depletion. The important difference is the depletion to be delayed at 650°C.

Only the solution-annealed samples and the samples aged at 650°C for 100 and 316 min are unsensitized but samples aged at 650°C for 10000 and 31622 min are heavily sensitized. Similarly, samples after 1000 min of ageing at 725°C are sensitized as well.

3.7. Analysis of Polarization Curves in Reverse Scanning. At the beginning of the reverse scanning, the anodic current density decreases, and the anodic curve moves to the left (Figure 7). This is an indication of thickening of the oxide film. On decreasing the potential, the anodic current density

FIGURE 9: Cathodic and anodic loops in DLEPR curve.

is reduced nearly to zero. This is due to the slowing of the anodic dissolution kinetics caused by thickening of the passive film. The sample has thus continued to passivate from E_{pass} through E_{rev} , back to potential E_3 . Further reducing the potential, the direction of the current density has changed between E_3 and E_4 as shown in Figure 9. It shows a loop consisting of cathodic current [23]. The origin of the cathodic current can be attributed to the fact that at potentials between E_3 and E_4 , the rate of the cathodic reaction is greater than the anodic current density, and hence the net current is cathodic over the potential range, $\Delta E (= E_3 - E_4)$ (Table 6). If the potential is further reduced on the reverse scan, the direction of the current density changes back, and an anodic reactivation loop is generated. This indicates that the oxide has dissolved, and metal dissolution reaction has occurred. The development of the reactivation peak current density (I_r) can be attributed to metal dissolution. The lowered reactivation peak current density I_r (on the reverse scan) is due to incomplete reactivation of the metal surface.

If no cathodic loop was generated on the reverse scan, the anodic reactivation would begin at a higher potential and would likely reach a high value of I_r in a short time, and thus the metal dissolution would take place.

The same cathodic loop behavior is observed on the reverse scans of polarization curves obtained from the solution annealed and aged samples by DLEPR test (Table 6).

The potential ranges (ΔE) of samples aged at 725°C from 100 and 31622 min where the cathodic loops are obtained, are different from that of the solution-annealed sample. In general, their reactivation curves look like that of the solution-annealed sample. A similar cathodic loop behavior has been observed for all cases but the anodic loops do not resemble that of the solution-annealed sample. This indicates that the precipitates developed in the microstructure influence the polarization behavior.

For all cases, the potential ranges (ΔE) for the cathodic loops change disorderly from 0.159 to 0.171 and are less than that of the solution-annealed sample. This means that the formation of the cathodic loop delays the occurrence of the anodic reactivation current loop for a short time. Then, the direction of the current density changes back quickly, and

TABLE 6: DLEPR test results on the reverse scans of polarization curves.

Temperature (°C)	Time (min)	E_3 (volt)	E_4 (volt)	$\Delta E (= E_3 - E_4)$ (volt)	I_r (mA/cm ²)	DOS ($I_r/I_a \times 100$)
Solution annealed at 1050°C, 1 hr		0.02521	-0.190090	0,215300	0.0063918	0.027634
	100	0.053818	-0.110000	0.163818	1.6857088	5.767805
	316	0.052163	-0.119650	0.171813	1.7231466	6.484404
Solution annealed at 1050°C, 1 hr + aged at 725°C	1000	0.060101	-0.103310	0.163411	22.5825614	53.421053
	3162	0.050114	-0.117800	0.167914	50.5214698	93.189389
	10000	0.063035	-0.108430	0,171465	50.4425582	90.422059
	31622	0.064701	-0.095247	0.159948	64.3463484	92.394528

the anodic reactivation current density begins to be generated at a potential of $E_4 = -0.110000$ V for ageing 100 min and at $E_4 = -0.119650$ V for ageing 316 min. It then reaches the peak value of $I_r = 1.6857088$ A/cm² with the DOS value of 5.76% for ageing 100 min, and $I_r = 1.7231466$ A/cm² with the DOS value 6.48% for ageing 316 minutes.

For the sample aged for 1000 min, the potential range for the cathodic loop is 0.163411 V. This is lower than the value measured for the solution-annealed one. The dissolution of oxide begins at a high potential such as $E_4 = -0.103310$ V. After a short delay, the reactivation current density increases to $I_r = 22.5825614$ A/cm². The DOS value is 53.42%.

For the sample aged for 3162 min, the range of the potential for the cathodic loop is 0.167914 V. This is higher than the value obtained for 1000 min of ageing. The E_4 ($= -0.117800$ V) has been found higher and E_3 ($= 0.050114$) lower with increasing ageing time. The reactivation peak current density (I_r) has reached 50.52146 mA/cm² corresponding to a high DOS value (93.18%).

For ageing time of 10000 and 31622 min, cathodic loops on the reverse scan are obtained within a potential range of 0.171465 and 0.159948 V, respectively. And then the anodic reactivation loops suddenly begin at higher potentials of E_4 such as -0.108430 and -0.095247 V. The reactivation peak current densities (I_r) have reached to 50.442 and 64.346 mA/cm², and the corresponding DOS values are 90.422 and 92.394%, respectively. This is because of the change in the microstructure. Due to longer ageing treatments the whole ferrite has transformed into σ and γ_2 . Dissolution of the secondary austenite results in greater weight losses and higher ratios of I_r/I_a . The higher anodic peak reactivation current density is the result of complete activation of the metal surface as evident by the high DOS values.

A similar behavior has been observed for the passive current densities (I_{pass}). The chromium depletion or dissolution of secondary austenite phase (γ_2) causes the passive current densities to shift to higher current densities as compared to that obtained from the solution-annealed sample (Figure 7, Table 5).

4. Conclusions

The effect of isothermal treatment at 725°C on the microstructures and consequent corrosion behavior of a duplex

stainless steel UNS S31803 was investigated. The important findings are summarized as follows.

(a) Only the solution-annealed sample was found unsensitized. The structure is free of precipitations, and consequently it presented a very small reactivation current. From the DOS values of specimens aged for 100 and 316 min., it may be concluded that these samples became less sensitized than those aged for longer ageing time. The degree of sensitization increases rapidly with increasing ageing time and this can be attributed to a higher contribution of chromium- and molybdenum-depleted areas resulting in the formation of the intermetallic phases.

(b) In a comparison to previous results [12], the sensitization of DSS was affected much by long-term ageing heat treatment at 725°C than that at 625°C.

(c) The DLEPR test showed that fine precipitates were insufficient to induce a significant susceptibility to intergranular corrosion. The role of chromium nitrides was less harmful because of the low amount of these precipitates.

(d) The intermetallic σ -phase has first precipitated at the interface of α/γ , α/α , and inside the α -ferrite grains up to 316 min ageing time. The σ -phase has then grown into coarse particles due to high diffusivity of chromium and molybdenum atoms in the ferrite matrix leaving behind a chromium-depleted zone named secondary austenite. The exposure of aged samples to iron-chloride acid media leads to a localized and selective attack on the secondary austenite.

(e) From the observations of the polarization curves it may also be concluded that cathodic loops do not affect metal dissolution. They merely delay the occurrence of anodic loops for a short time in a small potential range. These potential ranges (ΔE) over that cathodic loops are obtained depend on the protective film thickness, ageing temperature, time, and microstructural changes in the material. Actually, during the anodic sweep, the entire surface is active and contributes to the peak current. But during the reactivation sweep, only the sensitized areas contribute to the passive-active transition. So the oxide dissolves first, and then soon metal dissolution takes place.

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