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INVESTIGATION ON THE EFFECT OF ANNEALING TEMPERATURE ON THE INTERGRANULAR CORROSION SUSCEPTIBILITY OF AISI 409 FERRITIC STAINLESS STEEL

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Abstract. *Ferritic stainless steels are replacing austenitic grades in automotive applications due to a more attractive combination of material performance and cost. Welding operations are commonly employed as part of the manufacturing schedule of automotive parts. Depending on the time and temperature of thermal cycles to which the material is exposed, sensitization can take place due to precipitation of chromium carbides at grain boundaries, thus leading to intergranular corrosion. The aim of the present study was to investigate the intergranular corrosion susceptibility of the AISI 409 ferritic stainless steel submitted to different annealing conditions. The degree of sensitization (DOS) was determined using the double-loop electrochemical potentiokinetic reactivation (DL-EPR) method. Visual analysis was also undertaken by optical microscopy based on ASTM 763 practice W. The precipitates within the ferrite matrix were identified by scanning electron microscopy (SEM). The results showed that the material became more susceptible to intergranular corrosion after annealing at 600 °C, 650 °C and 900 °C. DL-EPR results were in agreement with the microstructural features observed after the tests based on practice W of ASTM 763.*

Keywords: *AISI 409 stainless steel, intergranular corrosion, DL-EPR*

1. INTRODUCTION

Ferritic stainless steels are used in automotive components in and structural applications due the low cost and corrosion resistance (Cashell and Baddoo, 2014). However, there are limitations regarding the weldability of these materials. Welding is employed as part of the manufacturing process of structures and automotive parts. Ferritic stainless steels without nickel present deleterious effects in the heat affected zone. Depending on the welding parameters, the grain can grow excessively and produce loss in fracture toughness, ductility, and corrosion resistance (Steigerwald, 1992; Krysiak *et. al.*, 1993). Intergranular corrosion can occur because of chromium depletion at grain boundaries caused by the precipitation of chromium-rich carbides immediately adjacent to the boundaries (Krysiak *et. al.*, 1993). This type of corrosion takes place when the corrosion rate of the grain boundary areas exceeds that of the grain interiors (Steigerwald, 1992).

Studies have been made about the intergranular corrosion in stainless steel using the double-loop electrochemical potentiokinetic reactivation (DL-EPR) test. In this method the degree of sensitization (DOS) is determined. The technique consists of anodic polarization from the open-circuit potential of the specimen up to its passive region. This is followed by reverse polarization to opposite direction back to the open-circuit potential (Scully, 1992; Taji *et. al.*, 2015). The DOS is determined by dividing the maximum current generated in the reactivation (reverse current density, I_r) to the maximum current generated in the activation (activation current density, I_a). When the steel is non-sensitized, the passive film remains almost intact during the reactivation current density and the reactivation polarization peak remains small. The greater the current, the lower the repassivation of the film due to chromium depletion at grain boundaries and more charge flowing over the metal surface.

The electrolyte used for DL-EPR tests generally consist of solutions with 0.5 - 2.5 M H_2SO_4 and 0 - 0.1 M KSCN, independently of the type of stainless steels. The test was originally developed for a concentration of 2.5 M H_2SO_4 in N_2 to austenitic stainless steel (Cihal and Stefec, 2001). Recently, Taji et al. (Taji *et. al.*, 2015) studied the effect of different tempering temperatures on the degree of sensitization and pitting corrosion of AISI 403 martensitic stainless steel using a modified DL-EPR solution (with the composition of 0.01 M H_2SO_4) and showed that the highest degree of sensitization and the lowest pitting potential occurred for the specimens tempered at 550 °C.

The effect of brief heat treatments within the 650 – 850 °C range on pitting corrosion and intergranular corrosion resistance of a lean duplex stainless steel was recently investigated (Zanotto *et. al.*, 2015). Using the DL-EPR method and anodic polarization curves a reduction of the pitting resistance and an increase of intergranular corrosion susceptibility of the lean duplex was observed for increasing temperatures, especially between 650 – 750 °C. A recovery of the pitting and intergranular corrosion resistance was observed at 850 °C due to redistribution of chromium to the depleted zones.

Bai et al. (Bai *et. al.*, 2015) investigated the intergranular corrosion behavior associated with evolution of delta-ferrite of Ti-modified Super304H austenitic stainless steel. The tests were carried out with DL-EPR. The author concluded that the precipitation of the sigma phase and $M_{23}C_6$ and a higher fraction of delta-ferrite with poor stability increased sensitization. This occurred at an annealing temperature of 650 °C. Prolonging the aging time beyond 48 h decreased the value of DOS due to diffusion of Cr atoms from the adjacent primary austenite phase to chromium-depleted regions. Similarly, Kim et al. (Kim *et. al.*, 2011) observed intergranular corrosion induced by Cr depletion zones formed due to Cr segregation around intergranular TiC in 409L ferritic stainless aged at 400, 500 and 600 °C.

In this paper the intergranular corrosion susceptibility of the AISI 409 ferritic stainless steel after different annealing conditions was studied using double-loop electrochemical potentiokinetic reactivation method and microstructure analysis by optical microscopy based on ASTM 763 practice W and scanning electron microscopy.

2. EXPERIMENTAL

2.1 Sample preparation

The material used in this work was a 2.0 mm thick cold-rolled, annealed AISI 409 ferritic stainless steel sheet. Its nominal chemical composition is shown in Tab. 1.

Table 1. Chemical composition (wt.%) of the AISI 409 stainless steel plate used in this work.

C	Mn	Si	P	S	Cr	Ni	N	Other
0.03	1.00	1.00	0.04	0.015	10.5 - 11.7	0.50	0.030	6(C+N)<Ti<0.50 Nb=0.17 máx.

The material was cut into small rectangular pieces with a plain area of approximately 1.0 cm^2. In order to obtain a homogeneous initial microstructure, the specimens were solution annealed at 1100°C for 30 minutes, followed by water quenching. Next, the specimens were annealed at 600, 650 and 900 ºC for 120 minutes and, then, water quenched. Heat treatments were conducted in a muffle furnace.

2.2 Electrochemical experiments

The working electrodes for the electrochemical measurements were prepared by electrically connecting the stainless steel samples to a copper wire by means of a colloidal liquid conductive silver paste and then embedding this set in epoxy resin. The exposed surface of each electrode was finished by wet-grinding with a series of emery papers from 200 to 2500 grit.

The DL-EPR tests were carried out using an Ivium nStat potentiostat/galvanostat. The experimental set-up consisted of a conventional three-electrode cell with Ag/AgCl as reference, a platinum wire as auxiliary electrode and the stainless steel sample as working electrode. The electrolyte used was a standard DL-EPR test solution (0.5 M sulfuric acid (H_2SO_4) + 0.01 M potassium thiocyanate (KSCN)).

Initially, the electrodes were cathodically polarized for 120 s at -1.0 V to remove the oxide film naturally formed on the surface. After that, the steady-state open circuit potential was reached in 300 s. The working electrode was anodically polarized from 0.0 mV vs. OCP to + 700 mV vs. OCP and then cathodically polarized from + 700 mV vs. OCP back to the OCP at a scan velocity of 1.67 mV/s.

2.3 Surface morphology

ASTM 763 practice W (ASTM, A763-15) was carried out for detecting susceptibility to intergranular attack. Following the method, the samples were immersed in 10 wt.% oxalic acid solution ($H_2C_2O_4 \cdot 2H_2O$). A stainless steel bar was used as cathode for the electrolytic etching. The samples were etched using a constant current of 1 $A.cm^{-2}$ for 90 s by means of D.C. power supply. The specimens were rinsed in hot water, washed with ethanol and dried ina hot air stream. Metallurgical microscope Zeiss AxioCam ICc5 was used to examine the etched surfaces. Samples without electrolytic etching were examined using a scanning electron microscope (Leica/Leo 440I) coupled with energy dispersive X-ray spectroscopy (EDS) detector to identify the precipitates within the ferrite matrix.

3. RESULTS AND DISCUSSION

3.1 Microstructural analysis

Figure 1 shows optical micrographs of the AISI 409 stainless steel samples after electrolytic etching in oxalic acid.

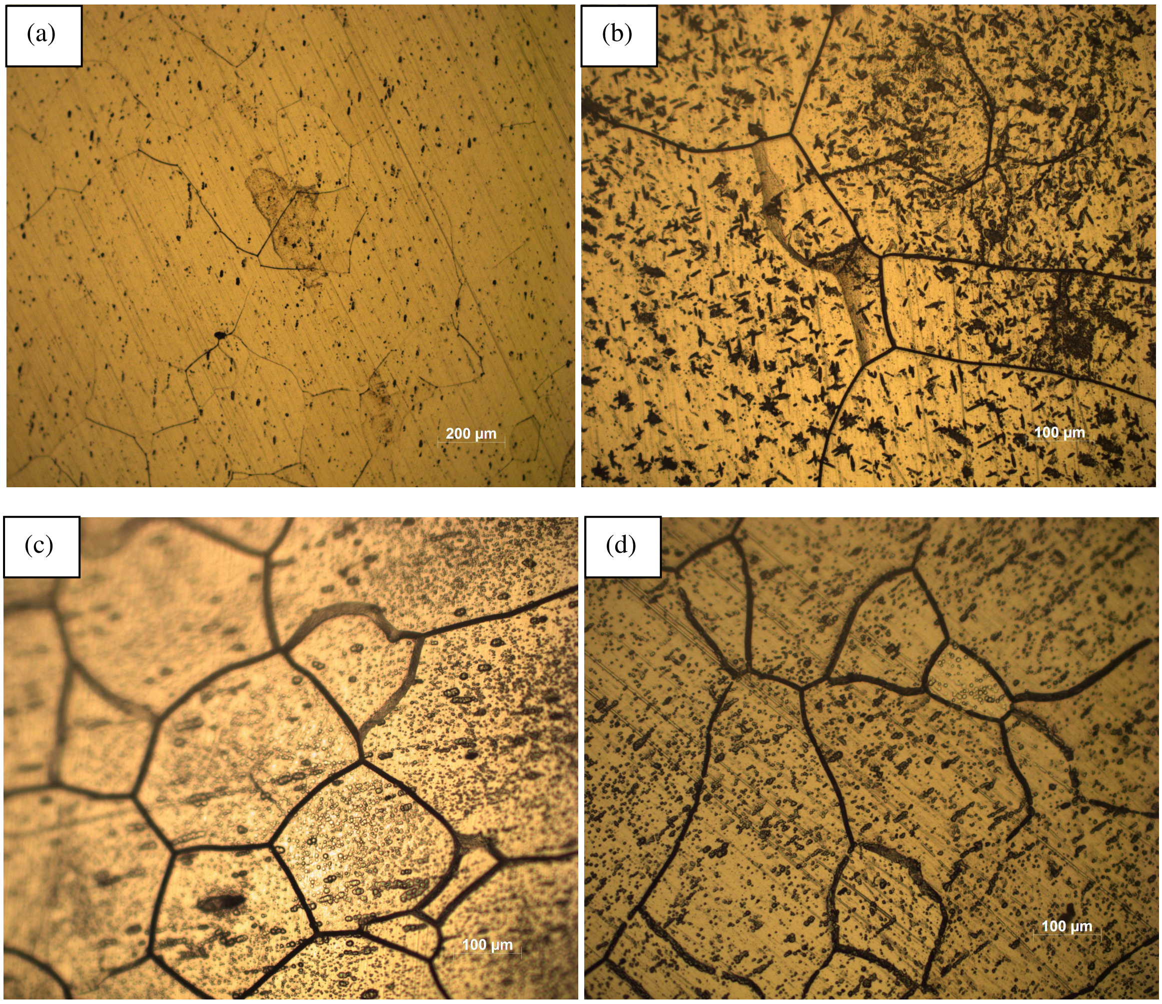

Figure 1. Micrographs of the AISI 409 stainless steel submitted to different heat treatments after the oxalic acid test: (a) solutionized; (b) annealing for 120 minutes at 600 ºC; (c) 650 ºC and (d) 900 ºC.

The oxalic acid dissolves the chromium rich phases (Serna-Giraldo, 2006) letting ditches in the microstructure. Thus, the microstructure that has ditches is sensitized. Fig. 1a presents a dual structure with some ditches but no single grain completely surrounded by them. The microstructures of annealed samples (Figs. 1b, 1c and 1d) show ditched structure caused by dissolution of carbides at grains boundaries.

SEM micrographs in backscattered electron imaging mode of the AISI 409 stainless steel samples submitted to different heat treatments are shown in Fig. 2. The micrographs reveal the presence of dark precipitates even at the solutionized state (Fig. 2a). It was not possible to distinguish between the different heat treatments with regard to the amount of precipitates formed at different annealing temperatures. One EDS spectrum of the region indicated by the white arrow in Fig. 2b revealed that three phases consisted of titanium-rich regions. Some authors (Kim *et al.,* 2009*;* Kim *et al.,* 2010) have also identified titanium carbides in 409-type stainless samples submitted to heat treatments at different temperatures and times. They observed that the intergranular corrosion resistance of this material was affected by the presence of the titanium-rich precipitates. The mechanism proposed for intergranular corrosion relies on the formation of chromium depleted zone around the titanium carbides and on chromium-carbides or chromium carbonitrides which is the most common cause of this phenomenon in ferritic stainless steels. Titanium has higher affinity for carbon than chromium. This would lead to the preferential formation of titanium carbides. As a result, unreacted chromium would segregate around the titanium carbide particles. Consequently, chromium would be depleted adjacent to these segregation regions giving rise to intergranular corrosion. The presence of titanium-rich precipitates is unequivocally shown in Fig. 2 and, thus, the mechanism proposed by Kim et al. can be active for our material.

Moreover, these authors show that ageing at 600°C can be critical for the onset of intergranular attack. However, the micrographs shown in Fig. 2 do not allow identifying significant microstructural differences between each heat treatment condition that could point to a clear dependence of intergranular corrosion with the annealing temperature.

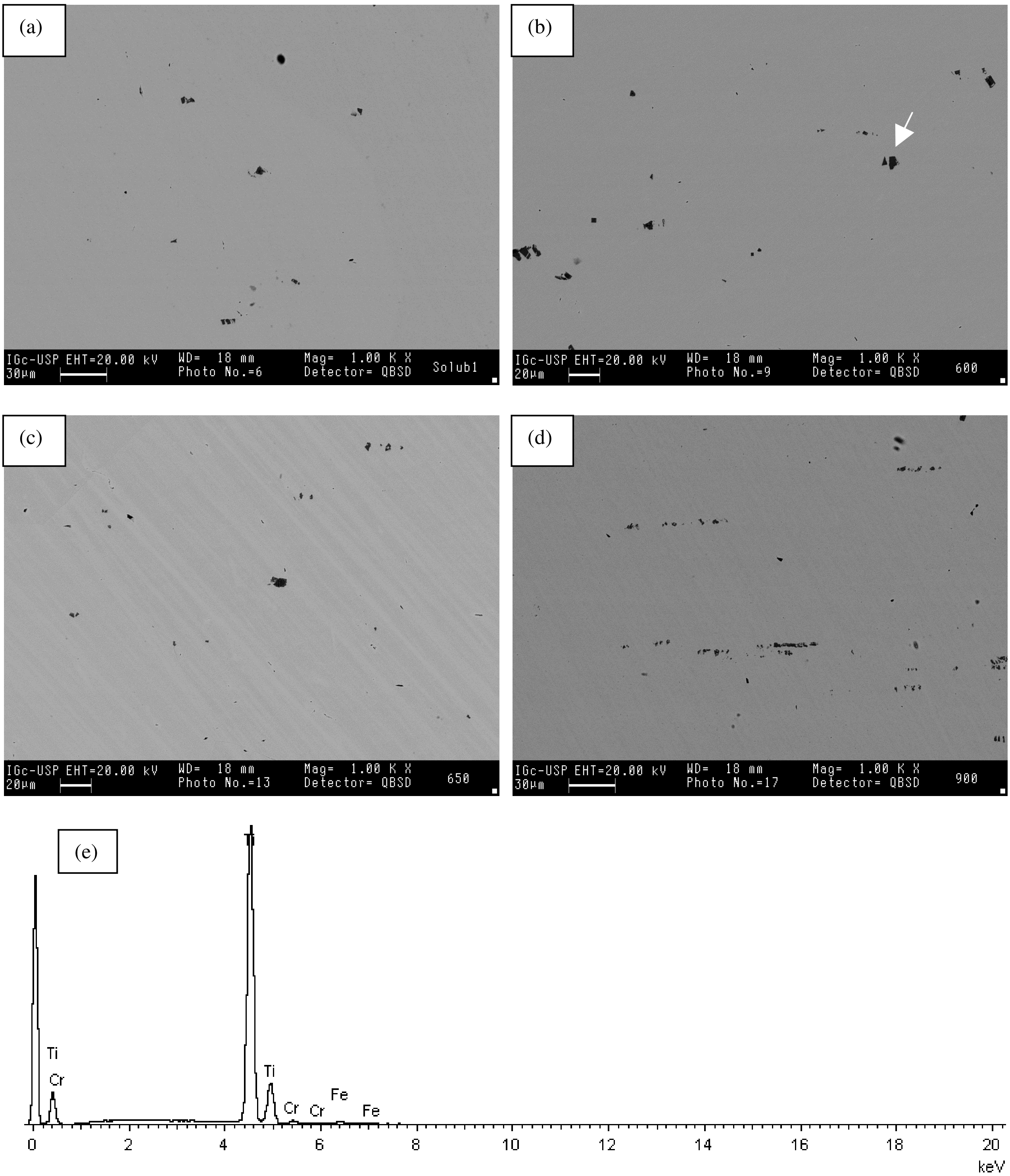

Figure 2. SEM micrographs of the AISI 409 stainless steel submitted to different heat treatmentst: (a) solutionized; (b) annealing for 120 minutes at 600 ºC; (c) 650 ºC and (d) 900 ºC; (e) EDS spectrum of region indicated in (b).

3.2 DL-EPR

DL-EPR curves for the AISI 409 stainless steel samples submitted to different heat treatments are shown in Fig. 3. The values of maximum activation current density (I_a) and maximum reactivation current density (I_r) were determined from these curves and are presented in Tab. 2 as well as the degree of sensitization (DOS) obtained by the ratio I_r/I_a. This ratio is used to quantify the susceptibility to intergranular corrosion of stainless steels.

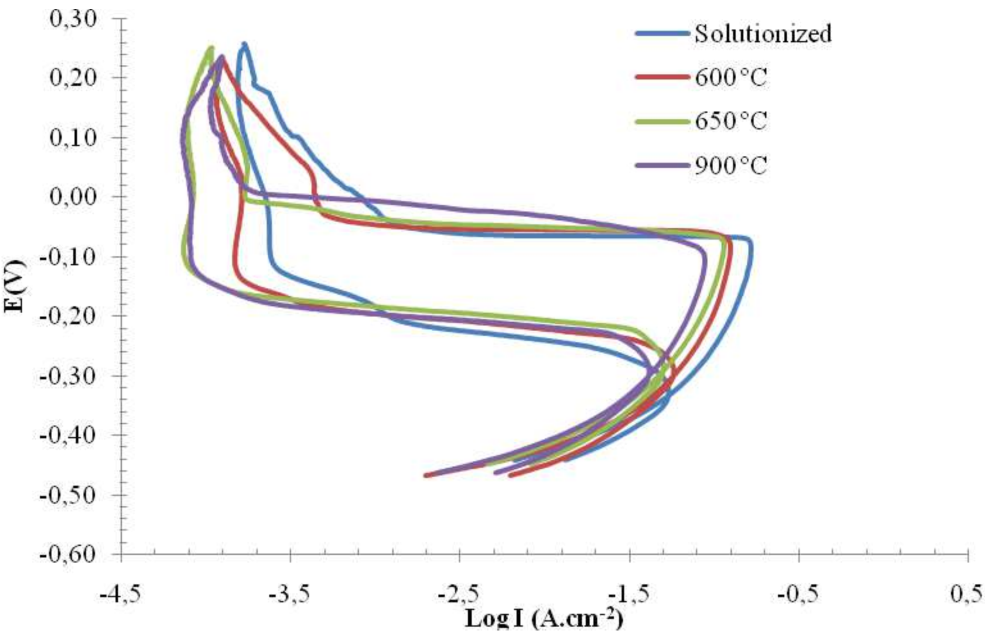

Figure 3. DL-EPR curves for the AISI 409 stainless steel samples submitted to different heat treatments.

Table 2. Currents and degree of sensitization values.

Treatment	I_r	I_a	DOS = I_r/I_a
solutionized	0,054	0,159	0,339
600 °C	0,126	0,058	0,462
650 °C	0,050	0,112	0,449
900 °C	0,042	0,088	0,474

The DL-EPR curves show typical features denoted by the increase of the activation current density up to the maximum value. From this point on, the current density decreases due the passivation of the electrode surface. During the reverse scan the passivated areas are reactivated due to the presence of intergranular precipitates and the passive film is locally broken, giving rise to increasing current densities up to the maximum reactivation current density peak (Buhler *et al.,* 2003). The results indicate that the solution treated condition has the lowest DOS, thus pointing to a lower susceptibility to intergranular corrosion. This result is expected, since the solution annealing is employed mainly to dissolve precipitates that could lead to grain boundary attack. For the aged samples the DOS increased with respect to the solution-treated condition. However, no clear relationship between DOS and annealing temperature could be perceived. This fact can be related to the microstructural features described in section 3.1. SEM micrographs did not indicate significant differences between the quantity and type of precipitates formed at each heat treatment condition. Furthermore, the microstructures after the oxalic acid test were characterized by ditched grains independently of the annealing condition whereas a dual structure was observed for the solutionized samples. In this regard, the oxalic acid test and the DL-EPR results are in good agreement, since the DOS value was effective at distinguishing between the solution-treated samples and the aged ones, but no clear trend could be identified for the samples aged at 600°C, 650°C and 900°C. The results shown in Tab. 2 suggest that there is a limiting DOS value for the occurrence of intergranular corrosion. Above 0,339 the microstructure of the AISI 409 stainless steel is typically sensitized whereas intergranular corrosion was not detected at this level. The AISI 409 stainless steel can be considered susceptible to intergranular corrosion when heated at 600°C, 650°C and 900°C. Manufacturing processes should avoid maintaining it for long times at these temperatures in order to prevent intergranular attack.

4. CONCLUSION

The oxalic acid test indicated sensitization after annealing at 600°C, 650°C and 900°C due to the formation of ditched grains. The solution-treated material presented a dual microstructure, being classified as non-sensitized according to practice W of ASTM 763. SEM micrographs and EDS analysis showed the presence of titanium-rich precipitates, independently of the heat treatment condition. No clear distinction between the amounts of precipitates could be detected for each condition. DL-EPR tests indicated that the degree of sensitization was increased after annealing at 600°C, 650°C and 900°C with respect to the solutionized material. The results obtained from the DL-EPR were in agreement with the microstructural features observed after the oxalic acid test.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

ASTM A763-15, 1979 “Standard Practices for Detecting Susceptibility to Intergranular Attack in Ferritic Stainless Steels”. ASTM International, West Conshohocken, PA, DOI: 10.1520/A0763-15.

Bai, G., Lu, S.; Li, D. and Li, Y., 2015. "Intergranular corrosion behavior associated with delta-ferrite transformation of Ti-modified Super304H austenitic stainless steel". *Corrosion Science*, Vol. 90, pp. 347-358.

Buhler H. E., Gerlach, L., Greven, O. and Bleck, W., 2003, “The electrochemical reactivation test (ERT) to detect the susceptibility to intergranular corrosion”. *Corrosion Science*, Vol. 45, pp. 2325-2336.

Cashell, K.A and Baddoo, N.R., 2014. “Ferritic stainless steel in structural applications”. *Thin-Walled Structures,* Vol. 83, pp. 169-181.

Cihal, V. and Stefec, R., 2001. “On the development of the electrochemical potentiokinetic method”. *Electrochimica Acta*, Vol. 46, pp. 3867-3877.

Kim, J.K., Kim, Y.H., Uhm, S.H.; Lee, B.H. and Kim, K.Y., 2009. “Intergranular corrosion of Ti-stabilized 11 wt% Cr ferritic stainless steel for automotive exhaust systems”. *Corrosion Science*, Vol. 51, pp. 2716-2723.

Kim, J.K., Kim, Y.H., Lee, B.H. and Kim, K.Y., 2010. “Effect of chromium content on intergranular corrosion and precipitation of Ti-stabilized ferritic stainless steels”. *Corrosion Science*, Vol. 52, pp. 1847-1852.

Kim, J.K., Kim, Y.H., Lee, B.H. and Kim, K.Y., 2011. “New findings on intergranular corrosion mechanism of stabilized stainless steels”. *Electrochimica Acta*, Vol. 56, pp. 1701-1710.

Krysiak, K.F., Grubb, J.F., Pollard, B. and Campbell, R.D., 1993. *Selection of Wrought Ferritic Stainless Steels*. ASM Handbook, Vol. 6, Welding, Brazing and Soldering, ASM International, USA, 9th edition.

Scully, J. R., 1992. *Electrochemical Methods of Corrosion Testing*. ASM Handbook, Vol. 13, Corrosion, ASM International, USA, 9th edition.

Serna-Giraldo, C.A., 2006. *Resistência à Corrosão Intergranular do Aço Inoxidável Ferrítico UNS S 43000: Avaliação por Método de Reativição Eletroquímica, Efeito de Tratamento Térmico e Mecanismo de Sensitização*. Escola Politécnica da Universidade de São Paulo, São Paulo.

Steigerwald, R., 1992. *Metallurgically Influenced Corrosion*. ASM Handbook, Vol. 13, Corrosion, ASM International, USA, 9th edition.

Taji, I., Moayed, M.H. and Mirjalili, M., 2015. “Correlation between sensitisation and pitting corrosion of AISI 403 martensitic stainless steel”. *Corrosion Science*, Vol. 92, pp. 301-308.

Zanotto, F., Grassi, V., Merlin, M., Balbo, A. and Zucchi, F., 2015. “Effect of brief heat treatments performed between 650 and 850°C on corrosion behaviour of a lean duplex stainless steel”. *Corrosion Science,* Vol. 94, pp. 38-47.

7. RESPONSIBILITY NOTICE