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Intergranular Corrosion of UNS S31803 Heat Treated at 800 °C Varying Range Times

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Abstract: The aim of this work is evaluate the intergranular corrosion on UNS S31803 steel, with heat treatments at 800 °C, varying treatment times of 30 mins, 360 mins and 1,440 mins. The results confirm the formation of σ phases and secondary austenite (γ_2). For the analysis of the influence of σ and γ_2 phases, metallographic analysis were conducted through optical microscopy, potentiokinetic reactivation electrochemical techniques and potentiodynamic polarization in NaCl 3.5% solution. Microstructural analysis has shown a formation of γ_2 and σ phase in heat treatment, due to diffusion of chromium and molybdenum from δ phase to γ phase, precipitating on δ/γ and δ/δ interfaces. The DL-EPR (Double loop electrochemical potentiokinetic reactivation) results have shown an increase of the DOS (degree of sensitization) for long periods of time on heat treatment. The results of potentiodynamic polarization showed a reduction of the corrosion and pitting potentials, followed by an increase of the current density when the UNS S31830 steel is heat treated during long periods of time.

Key words: Intergranular corrosion, σ phase, DL-EPR, pitting corrosion.

1. Introduction (Word Style (Times New Roman))

DSS (Duplex stainless steel) are being used in oil and gas industries, cellulose and marine industries, because of its excellent mechanical strength, high tenacity and corrosion resistance [1, 2]. Besides those advantages, DSS are submitted to sensitization when exposed to a number of high temperatures between 300-900 °C, with the formation of numerous deleterious phases, such as carbides (MC, M_6C, M_7C_3, $M_{23}C_6$), chromium nitrides (Cr_2N), σ phase and χ phase. In smaller time ranges, σ phase precipitates on δ/γ *e* δ/δ interfaces, which affects the DSS properties, being the σ phase a very hard and brittle intermetallic compound [3, 4]. Elevated levels of chromium and molybdenum may promote the σ phase formation, which occurs during processes that involve heat treatment, plastic deformation or yet due to aging [5]. The objective of this work is to observe the influence of the σ phase on UNS S31803 steel concerning its corrosion resistance.

2. Experiments

2.1 Preparation of Samples

The samples were obtained by Villares Metals S/A, hot rolled in solubilization heat treatment conditions. After that, samples were cut in 15 × 20 × 2 mm^3 and heat treated at 1,100 °C for 1 h, followed by water cooling, so that all residual stresses and possible deleterious phases are solubilized. Once this is done, these samples were aged at 800 °C for 30 mins, 360 mins and 1,440 mins, to precipitate different amounts of σ phase. The chemical composition of UNS S31830 steel is shown in Table 1.

The samples were submitted to metallographic characterization through sanding on #400 and #1200 sandpaper and polishing on Al_2O_3 with particles between 1.0 μm and 0.3 μm. Then the samples were washed with distilled water and ethanol, and dried with hot air. After that, the samples were attacked chemically

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Table 1 Chemical composition of UNS S31803 (wt.%).

C	Mn	Si	Cr	Ni	Mo	N	Fe
0.04	1.45	0.39	22.50	5.18	3.48	---	bal.

in Behara’s solution (20 ml HCl + 80 ml distilled water + 1.0 g $K_2S_2O_5$), this being an agent utilized to reveal *δ*, *γ* and *σ* phases. The samples were examined through an optical Motic 102 M microscope.

2.2 DL-EPR (Double Loop Electrochemical Potentiokinetic Reactivation)

DL-EPR (Double loop electrochemical potentiokinetic reactivation technique) was conducted to determinate the DOS (degree of sensibilization) of the samples. A setup of three electrodes, including UNS S31803 as working electrode, platinum electrode as counter electrode and SCE (saturated calomel electrode) as reference electrode, in an electrochemical cell containing a solution of 2 M of H_2SO_4 + 1.5 M HCl [6]. The exposed surface area of the working electrode was of 0.389 cm^2. For the DL-EPR test, a IVIUM portable potentiostat was utilized for an analysis tax of 1.667 mV/s at a temperature of 30 ℃ ± 0.1 ℃. The samples were polarized from E_{ocp} for 300 seconds to obtain the steady-state potential. After that, the measures was obtained from E_{ocp} to E_{ocp} + 1.00 V_{sce} in anodic direction, returning to the E_{ocp} potential, as described by ISO 12732 standard [7].

2.3 Potentiodynamic Polarization in NaCl 3.5%$_{wt.}$

Potentiodynamic polarization were conducted following the same electrode configuration of the DL-EPR tests, in an NaCl 3.5% solution (simulated seawater), at room temperature, in order to obtain the cathodic/anodic behavior, the formation of the passive layer and the corrosion and pitting potentials of the samples. Before the realization of the polarization measurements, E_{ocp} was measured for 60 mins so that the potential of the whole system could be established in steady-state. The scan rate was 1.667 mV/s, varying the potential in 10 mV of the cathodic potential, in relation to E_{ocp}, to +1.50 V anodic potential, in order to evaluate the formation and protection of the Cr_2O_3 passive layer.

3. Results and Discussions

3.1 Microstructural Analysis

Figs. 1-4 show the microstructures of the UNS S31830 steel as received and heat treated at 800 ℃ for 30 mins, 360 mins and 1,440 mins, respectively. The microstructures shows a fraction of austenite slightly superior to the ferrite [8]. Fig. 1 shows the microstructures of two phases, which consist of *δ* ferrite and *γ* austenite. In Figs. 2 and 4, the dark region represents *δ* phase, gray region represents *γ* phase and white region represents *σ* phase.

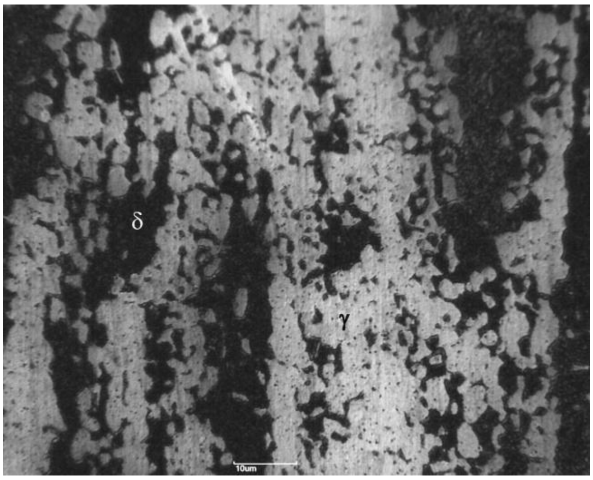

Fig. 1 Microstructure of UNS S31803, as received.

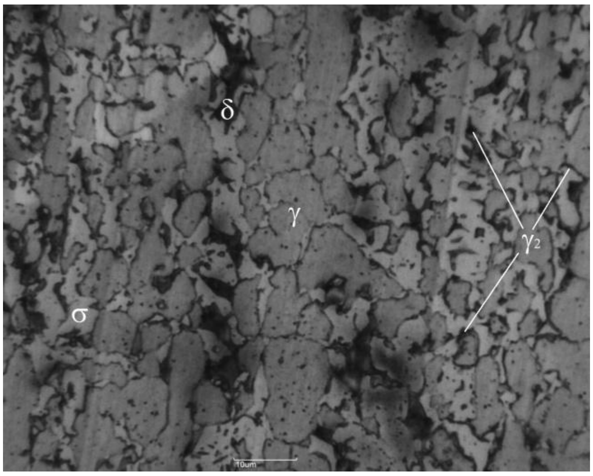

Fig. 2 Microstructure of UNS S31803, heat treated for 30 mins.

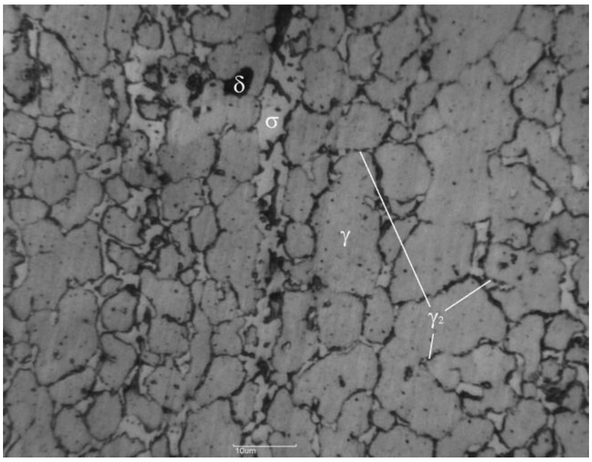

Fig. 3 Microstructure of UNS S31803, heat treated at 360 mins.

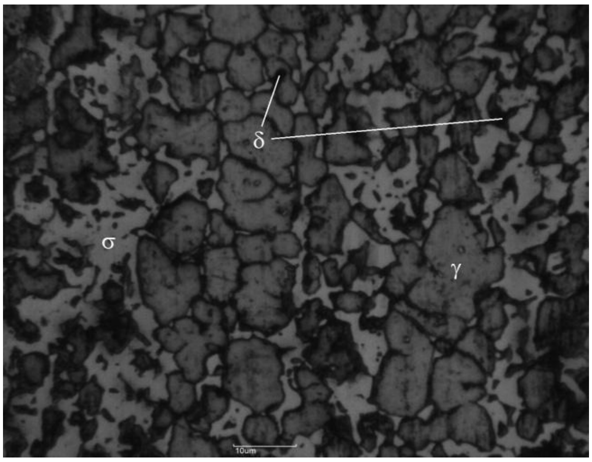

Fig. 4 Microstructure of UNS S31803, heat treated at 1,440 mins.

The realization of heat treatments in time intervals of 30 mins and 250 mins, according to the observed on Figs. 2 and 3 allow an observation the beginning of the $\delta \rightarrow \sigma + \gamma_2$ transformation, showing the presence of δ ferrite and γ austenite, followed by the precipitation of the σ phase along the δ/γ and δ/δ grain boundaries, where these interfaces are known as the σ phase preferential nucleation sites. Figs. 2 and 3 also show the formation of γ_2 secondary phases between the σ/γ interface inside the σ phase. This phase is called secondary austenite, and precipitates on temperatures ranging from 600 ℃ to 1,000 ℃, in a time lapse of 30-240 mins [9]. Fig. 4 shows the formation of δ ferrite, γ austenite and σ phase, without precipitation of secondary austenite, because in heat treatments for long periods of treatment, the σ phase formation kinetic is more favored, with the reduction of the γ_2 phase, being the γ_2 phase kinetically favored only for short time periods [10].

3.2 DL-EPR Results

Figs. 5-8 show the data obtained on DL-EPR tests for the UNS S31803 steel heat treated after solubilization (Fig. 5) and with heat treatment at 800 ℃ for 30 mins, 360 mins and 1,440 mins, respectively (Figs. 6-8). The results show a progression on the I_r/I_a ratio increase. On the case of Fig. 5, no sensitization was observed, since the heat treatment at 1,100 ℃ promoted the solubilization of the main elements of the alloy, those being chromium and molybdenum, with the following reorganization of the crystallyne structure [11]. A small sensitization is observed at the sample treated for 30 mins, indicating the formation of σ and γ_2 phases on UNS S31830 steel. As noted by many authors, σ phase precipitates on grain boundaries of δ/γ and δ/δ [3-6, 9, 10].

Figs. 7 and 8 show an increase of the I_r/I_a ratio for heat treatment in larger time. These results suggest that the formation of the σ phase is promoted in larger time lapses, once the σ phase nucleation kinetic is favored on heat treatment in large time lapses, with consequent elimination of the secondary austenite [12]. Fig. 8 shows, in a potential close to +0.45V, the appearing of a second peak of reactivation, with a moderate current intensity, which suggests a uniform

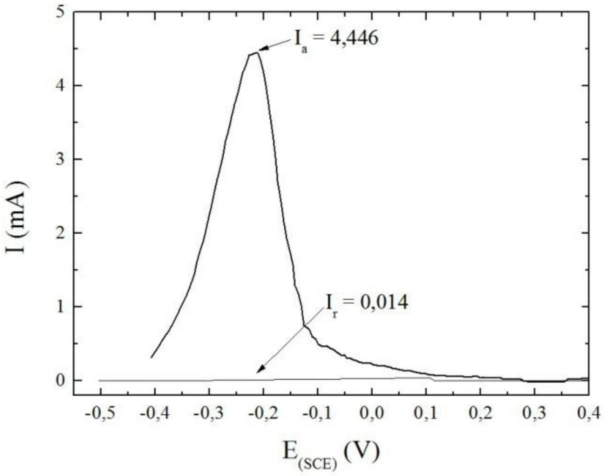

Fig. 5 DL-EPR test of UNS S31803, as received.

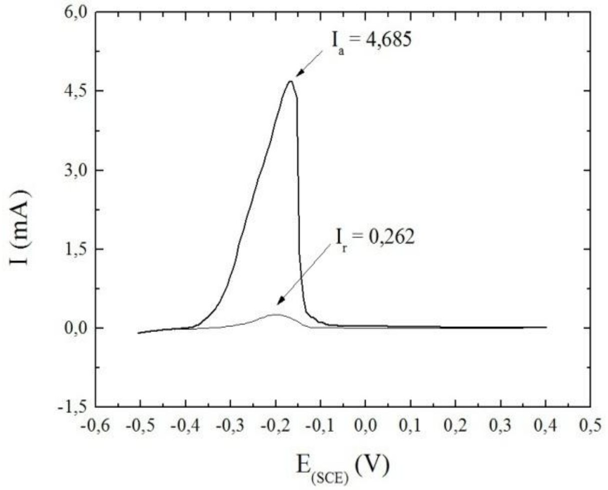

Fig. 6 DL-EPR test of UNS S31803, heat treated for 30 mins.

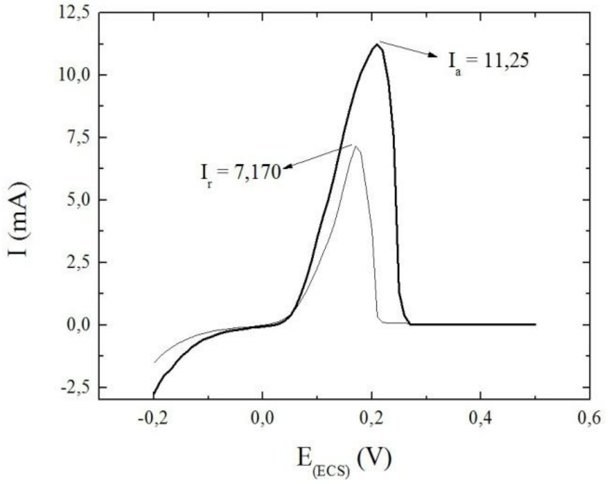

Fig. 7 DL-EPR test of UNS S31803, heat treated at 360 mins.

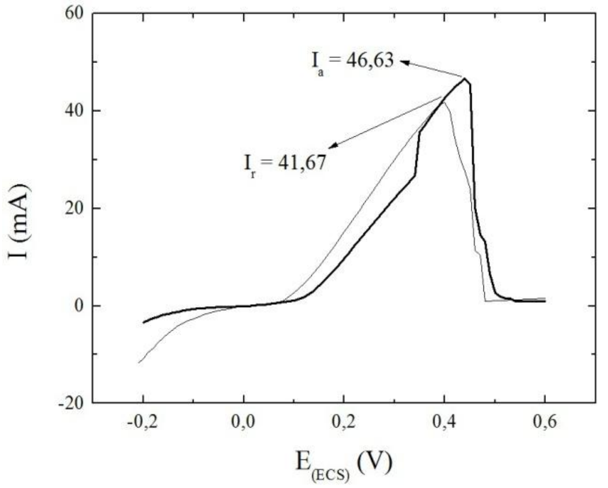

Fig. 8 DL-EPR test of UNS S31803, heat treated at 1,440 mins.

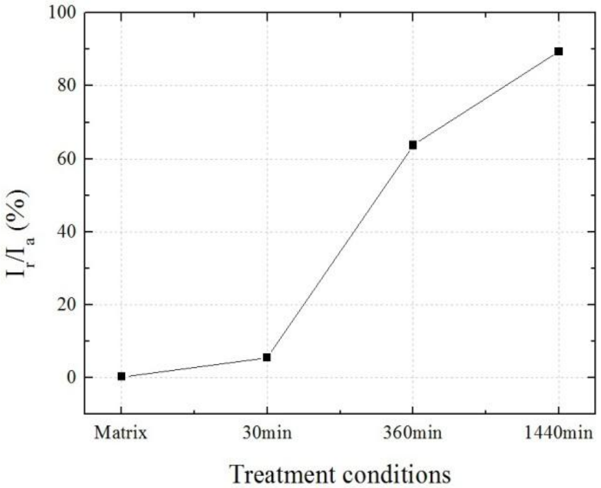

Fig. 9 I_r/I_a values obtained from the heat treated UNS S31803 samples.

corrosion peak, followed by a pitting corrosion of *γ* phase [13]. Fig. 9 shows the increase of the I_r/I_a current ratio on heat treatment. Results confirms that the DL-EPR tests depends on the chromium depleted regions and, consequently, on the precipitations, especially when it comes to *σ* phase.

3.3 Potentiodynamic Polarization in NaCl 5%.

Figs. 10 and 11 show the behavior of UNS S31830 steel in NaCl 3.5% with the formation of the Cr_2O_3 passive layer (Fig. 10) and pitting formation (Fig. 11), analysing the heat treatment of the samples. The increase of the heat treatment times shows a slight decrease of the corrosion potential (E_c) and also of the pitting potential (E_p), reducing the pitting corrosion resistance of the UNS S31830 steel. In Fig. 10, in a potential close to 0.00 V, the sample as received (matrix) and heat treated for 30 mins show a behavior similar on the Cr_2O_3 passive layer formation, while the samples which were heat treated for 360 mins and 1,440 mins presents a significant increase in current density [14, 15]. These results suggests that the heat treatment for long time lapses reduce the formation of the passive layer, once the available chromium for the formation of the passive layer is precipitated on *σ* phase, establishing that inappropriate heat treatments may damage the UNS S31830 corrosion resistance.

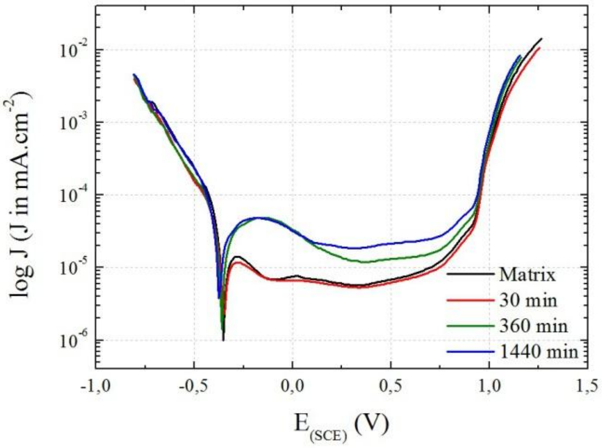

Fig. 10 DL-EPR test of UNS S31803, as received.

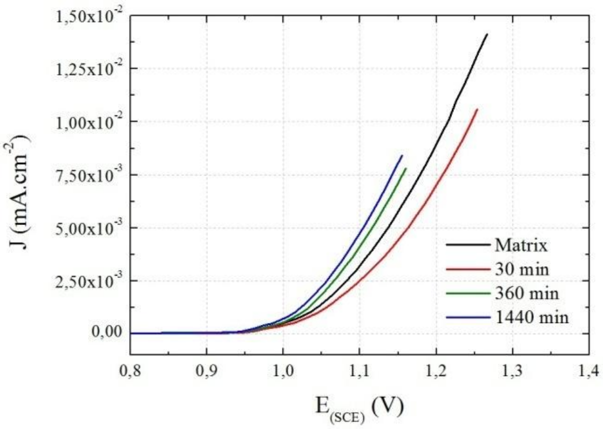

Fig. 11 DL-EPR test of UNS S31803, heat treated for 30 mins.

Precipitation of σ phase can be explained by the reduction of chromium and molybdenum in regions next to the increase of σ phase [15], In Fig. 11, the σ phase effect on δ/γ and δ/δ interfaces show a decrease of the pitting potential, when imposed to heat treatment during long time lapses.

Matrix sample and heat treated sample for 30 mins shows the same pitting potential, followed by a reduction of E_p on samples which were heat treated for 360 mins and 1,440 mins. For the sample heat treated for 30 mins, a quick deterioration is observed, suggesting to be an effect of the γ_2 formation, since this phase is formed on chromium depleted regions on σ phase, because the chromium and molybdenum diffusion is inferior on γ_2 phase, when compared to δ phase [16]. For the samples heat treated for 360 mins and 1,440 mins, it is suggested that the decrease of the pitting potential and increase of current density on UNS S31830 steel is due to fact of an increase of σ phase, containing elevated concentrations of chromium and molybdenum, reducing the formation of a Cr_2O_3 passive layer [14-16].

4. Conclusions

With the realization of this work, it was possible to observe that heat treatments for long periods promotes a greater diffusion of chromium and molybdenum from δ to γ, forming δ phase and secondary austenite (γ_2), when γ_2 is the attacked phase, especially by localized corrosion, followed by δ phase. DL-EPR results confirms that long time periods of heat treatments promotes a formation of δ phase, observed by increase of DOS on UNS S31803. Lastly, the UNS S31803 steel is more susceptible to localized corrosion for long time periods of time on heat treatments, due to the high content of chromium and molybdenum present on these steel, favoring the γ_2 and δ phases precipitation, reducing the Cr_2O_3 passive layer formation.

Acknowledgments

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