

Pedro Rupf Pereira Viana^{1*}, Luiza Venturini² and Yasmin Siqueira Souza²

Metallurgical and Materials Engineering Departament, Federal Institute of Espírito Santo, Vitória-ES 29040-780, Brazil
 Chemical Engineering Departament, Pitágoras College, Linhares-ES 29901-398, Brazil

Abstract: Austenitic stainless steels, when exposed to welding conditions or aging for length of service, it's observed the formation of numerous deleterious phases, such as several kinds of carbides type MC, M_6C , M_7C_3 , $M_{23}C_6$, and intermetallic secondary phases (sigma, chi, laves), which cause the process of intergranular corrosion. The aim of this work was verifying the formation of the types of carbides and/or intermetallic phases existing in the stainless AISI 304 at 800 °C, varying the timing of heat treatment between 30, 360 and 1,440 min. The optical microscopy analysis revealed the predominant formation of the carbide type $M_{23}C_6$. The results of DL-EPR (double loop electrochemical potentiokinetic reactivation) tests showed a gradual increase in the precipitation of this carbide with the increase of treatment time. The potentiodynamic polarization showed that the precipitation of this carbide reduce the formation of the Cr_2O_3 passive layer, suggesting that the precipitate carbide to be predominantly of the $Cr_{23}C_6$ type.

Key words: Intergranular corrosion, M₂₃C₆, DL-EPR, pitting corrosion.

1. Introduction

Austenitic stainless steels are the most common among stainless steels and are characterized by an excellent corrosion resistance, high strenght and good weldability. The austenitic structure is stabilizing at room temperature, due to nickel and manganese addition [1, 2]. However, it is not only the austenitic matrix that determine the property of these materials, since numerous phases, such as δ -ferrites, carbides, intermetallic phases, borides, sulfides, nitrides and martensites induced through deformation may be present in the microstructure of those steels. Regarding corrosion, mainly intergranular corrosion, it is a kind localized in metallic materials which present crystalline defects (gaps, discordances and grain boundaries) and chemical heterogeneities (precipitates, inclusions and microsegregations). Depending on the potential of the crystallyne defects and/or the present chemical heterogeneities, stainless steel might be attacked primarily through grain boundaries [3, 4]. Among the current types of corrosion, intergranular corrosion is, beyond doubt, the most dangerous and deteriorative of all, since it is visible only in microscopic form, promoting the spread of cracks, compromising structures and devices. Through various tasks, austenitic stainless steel might endure intergranular corrosion or sensitization when exposed to temperatures above 500 °C, with precipitation of MC, M_6C , M_7C_3 , $M_{23}C_6$ (M = Cr, Mo, Fe) carbides and sigma, chi and Laves phases on grain boundaries [5-7]. With the formation of those carbides and intermetallic phases, which present high chromium and molybdenum percentages in their composition, steel becomes yet more vulnerable to corrosion when amidst SO₂, NO_X, e, and Cl⁻ ions, because the Cr₂O₃ passive layer formation on austenitic and duplex stainless steel ends up being compromised, since the chromium concentration present in these steels is reduced [8].

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2. Experimental Sections

2.1 Preparation of Samples

The samples were obtained by Villares Metals S/A,

^{*}**Corresponding author:** Pedro Rupf Pereira Viana, Prof./M.Sc., research filed: corrosion. E-mail: pedrorupf@gmail.com.

hot rolled. The samples were cut on $15 \times 20 \times 2 \text{ mm}^3$. proportion, then submitted to solubilization heat treatment at 1,100 °C for 1 h, followed by quenching in water, in order to remove all residual tension from the rolling process, as well as the elimination of an pre-existing deleterious phase in the steel. After the solubilization heat treatment, the samples were heat treated at 800 °C for 30, 360 and 1,440 min, to induce the precipitation of different amounts of carbides on AISI 304 steel grain boundaries. Chemical composition of AISI 304 is shown in Table 1.

The samples were then submitted to metallographic characterization through sanding using sandpapers between 320 to 1,200 mesh, followed by polish in Al₂O₃ solution, with particle sizes between 1.0 and 0.3 um, ending the preparation of samples by washing them in distilled water and ethanol, drying in hot air. After preparation, the samples were electrochemically attacked in a 10 wt% aerated solution of oxalic acid, this being an agent which selectively attacks $M_{23}C_6$ precipitated and MC types. Following the electrochemical attack, samples were washed in distilled water, dried in hot air and observed through a Motic102M optical microscope.

2.2 DL-EPR (Double Loop Electrochemical Potentiokinetic Reactivation)

The DL-EPR test was realized to determine the DOS (degree of sensitization) of the samples. A configuration of three electrodes was used, where the samples used as work electrode, a platinum electrode as counter electrode and SCE (saturated calomel electrode) as reference electrode in an electrochemical cell containing oxalic acid solution at 10 wt%, as indicated by Čihal et al. [9] and the ASTM G108 Standard [10]. For the double loop electrochemical potenciokinetic reactivation test, an IVIUM portable potentiostat, previously polarized in open circuit potential (E_{ocp}) for pre-treatment in 300 s, at scanrate of 1.5 mV·s⁻¹ at temperature of 30.0 °C ± 0.1. The samples were polarized from E_{ocp} potential to the

Table 1 Chemical composition of AISI 304 (wt%).

С	Mn	Si	Cr	Ni	Мо	Ν	Fe
0.04	1.35	0.41	18.05	8.83	0.03		bal.

 E_{ocp} + 800 mV_{ECS} potential at anodic direction, followed by a reverse polarization until E_{ocp} potential, as sugested by ISO 12732 Standard [11].

2.3 Potentiodynamic Polarization in NaCl 3.5 wt%

The potentiodynamic polarization measurements were conducted according to the same configuration utilized on the electrochemical potentciokinetic reactivation tests in a NaCl 3.5 $\%_{m/V}$ solution (simulated sea water), at room temperature, in order to obtain the cathodic/anodic behavior, formation of passive Cr₂O₃ layer and pitting potential. Before the realization of the polarization measures, the open circuit potential was measured for 3,600 s, in order to stabilize the potential of the samples. The scanrate utilized was 1,667 mV·s⁻¹, according to the ASTM G61 Standard [12], until the +1.50 mV potential, in order to assess the formation and protection of the passive layer, as well as the determination of the pitting potential of the samples.

3. Results and Discussion

3.1 Microstructural Analysis

Figs. 1-4 show the microstructures of AISI 304 as received and heat treated at 800 °C for 30, 360 and 1,440 min, respectively.

The microstructures show a predominant austenite phase, and in Figs. 2-4, a formation of $M_{23}C_6$ type carbides in grain boundaries. Fig. 2 shows a slightly formation of $M_{23}C_6$ dual precipitation type, according to the ASTM A262 Standard [13]. Figs. 3 and 4 show a higher formation of $M_{23}C_6$ type carbides in grain boundaries, with dual and ditch type precipitates. These results confirm that the heat treatments in AISI 304 promote a high depletion of chromium in these alloys, as noted by several authors [14-17].



Fig. 1 Microstructure of AISI 304, as received.



Fig. 2 Microstructure of AISI 304, heat treated for 30 min.



Fig. 3 Microstructure of AISI 304, heat treated for 360 min.

3.2 DL-EPR Results

Fig. 5 shows the result obtained by the DL-EPR method on AISI 304 steel, as received. Result shows that this sample did not suffer any kind of formation of $M_{23}C_6$ type of precipitates on the grain boundaries because, according to Čihal et al. [9] and the ISO



Fig. 4 Microstructure of AISI 304, heat treated for 1,440 min.



Fig. 5 DL-EPR test of AISI 304, as received.

12732 standard [11], the ratio I_r/I_a , which corresponds to the maximum values of reactivation current and activation current, respectively, has a value close to zero. According to ISO 12732 [11], it is considered that the values of $I_r/I_a < 0.01$, steel is considered as non-sensitized. To I_r/I_a ratios where the value is between $0.01 < I_r/I_a < 0.05$, steel is partially sensitized and, lastly, values of $I_r/I_a > 0.05$, steel is fully sensitized. Figs. 2-4 illustrate the result of the heat treated samples at 30, 360 and 1,440 min, respectively.

According to observed on Figs 1-4, there is a reduction of the activation current values (I_a), followed by an increase of the reactivation current values (I_r), these being similar to the ones observed by many authors [5, 8, 13-16]. These results show that the AISI 304 steel samples become more susceptible

to intergranular corrosion, when subjected to heat treatment. Fig. 1 shows that the realization of solubilization heat treatment for elimination of possible deleterious phases precipitated on grain boundaries and residual tension from the rolling process was efficient, showing a I_r/I_a ratio value close to 0.0054, characterizing that the steel is no sensitized, and so no showing the formation of $M_{23}C_6$ type carbides on grain boundaries, which promotes intergranular corrosion. Fig. 9 shows the evolution of I_r/I_a ratio in function of the treatment conditions, showing the sensitization level of the samples.

Based on Fig. 5 result, it is observed that the sample treated at 800 °C for 1,440 min presents the highest sensitization level, not only for the relation, but also because of the formation of the ditch type precipitates which, according to ASTM A262 Standard [13], it is a precipitate that creates deep holes around the grain boundaries, accentuating the intergranular corrosion. On Della Rovere et al. [15], it was found that in a AISI 304 steel, heat treated in a range of 650-750 °C, suffers strong intergranular corrosion, presenting ditch type precipitate along its microstructure.

3.3 Potentiodynamic Polarization in NaCl 3.5 wt%

Fig. 10 shows the behavior of the passive Cr_2O_3 layer formation from the AISI 304 steel samples as received and heat treated for 30, 360 and 1,440 min, while Fig. 11 shows the behavior of the samples, in the same conditions, regarding the behavior of the pitting corrosion formation.

The increasing of the heat treatment time on AISI 304 steel show the reduction of the corrosion potential (E_c) and the pitting potential (E_p), decreasing the pitting corrosion resistance on the samples. On Fig. 6 and also on Fig. 7, for the 0.00 V potential, the samples as received presents an excellent formation of the passive Cr₂O₃ layer, while on the samples that went through heat treatment for 30, 360 and 1,440 min, the current density presents a considerable increasement, within the analyzed potential range. These results

suggest that long period heat treatments decrease the passive Cr_2O_3 layer formation capacity, since the chromium available for the passive layer formation



Fig. 6 DL-EPR test of AISI 304, heat treated for 30 min.



Fig. 7 DL-EPR test of AISI 304, heat treated for 360 min.



Fig. 8 DL-EPR test of AISI 304, heat treated for 1,440 min.



Fig. 9 Ir/Ia values obtained from the heat treated AISI 304 samples.



Fig. 10 AISI 304 samples polarization curves as received and heat treated for 30, 360 and 1,440 min, respectively, showing the formation of Cr₂O₃ layer.



Fig. 11 AISI 304 samples polarization curves as received and heat treated for 30, 360 and 1,440 min, respectively, showing pitting corrosion formation.

precipitates in the form of $Cr_{23}C_6$, demonstrating that inappropriate heat treatment and/or aging time compromise the resistance to corrosion of this steel, mainly when the environment is rich in chlorides. This significative E_c reduction, as steel heat treatment time increases occurs, first of all, due to the formation of the M₂₃C₆ type carbide precipitates, which potentialize the corrosive attack on grain boundaries, as observed on the works of Ghosh et al. [7] and Deng et al. [18]. A preponderant factor which occurs on AISI 304 steel, when compared to AISI 316 steel, is the fact that AISI 304 steel does not present any molybdenum in its composition, different from AISI 316 steel, which has about 3-5 wt% molybdenum in its composition. According to Souza [19], molybdenum is an alloying element that favors increasement of the austenitic stainless steel corrosion resistance in the presence of chlorides, what grounds the fact that precipitates are formed by $Cr_{23}C_6$ reducing, then, the passive Cr_2O_3 layer formation and protection capacity against corrosion on the heat treated samples of this work.

On Fig. 7, it can be noticed on the potential range close to +0.20 V that the sample as received has a slightly increasing of its current density. According to Deng et al. [18], these are current transients, during the formation of metastable character pitting, where these metastable pitting are nothing more than the beginning of pitting formation on defective regions of the surface, having its origin on the adsorption of the electrolyte on steel surface.

The results of the heat treated AISI 304 steel samples also presented those fluctuations on current densities, suggesting that heat treatment influenced not only on the formation of $M_{23}C_6$ type carbides and of other secondary phases, but also influence on the reorganization of the crystal structure of the studied steel, suggesting that it is possible to occur increase of the Gibbs free energy on the grain/surface interface, favoring the adsorption of the electrolyte on the surface of steel with the increasing of temperature and/or the heat treatment time, as well as the grain/grain interface, on two aspects: the first aspect due to the fact that the secondary phases precipitation generate a large number of discordances, according to Wasnik et al. [20], Sieurin [21], and Tavares et al. [22], fostering the pitting formation; the second aspect comes from the fact that the grain reorganization increase the thermal and electrical conductivity of the AISI 304 steel, leading to increased current density of the of the heat treated steel, in relation to their respective matrix, according to the related on Buscail et al. [23] and Arjmand [24] works.

4. Conclusions

With the realization of this work, it was possible to observe that heat treatments through long time periods promote high diffusion of the chromium along the AISI 304 structure, causing the intergranular corrosion on this steel. The DL-EPR test results confirm that long periods of heat treatment promote the $Cr_{23}C_6$ formation, being noted in this result an increase on the sensitization level of the AISI 304 steel, through a growth of the Ir/Ia ratio. Lastly, the potentiodynamic polarization results have shown that the heat treated samples of the AISI 304 steel presented reduction in their respective corrosion potentials, as well as they have become more susceptible to pitting corrosion, due to the fact that a large quantity of chromium present in these steel precipitates in the form of $Cr_{23}C_6$ on grain boundaries, reducing the capability of formation and protection of the passive Cr₂O₃layer.

Acknowledgments

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