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# Sensitization evaluation of the austenitic stainless steel AISI 304L, 316L, 321 and 347

A. S. LIMA, A. M. NASCIMENTO
*Departamento de Engenharia Mecânica, Universidade Federal do Ceará, Campus do Pici, Bl. 714, 60455-900 Fortaleza, Ce, Brazil; Departamento de Química Analítica e Físico-Química, Universidade Federal do Ceará, C.P. 6035, 60455-970 Fortaleza, Ce, Brazil*

H. F. G. ABREU
*Departamento de Engenharia Mecânica, Universidade Federal do Ceará, Campus do Pici, Bl. 714, 60455-900 Fortaleza, Ce, Brazil*

P. DE LIMA-NETO*
*Departamento de Química Analítica e Físico-Química, Universidade Federal do Ceará, C. P. 6035, 60455-970 Fortaleza, Ce, Brazil*
*E-mail: pln@ufc.br*

This work presents a systematic investigation of the influence of time and temperature in the sensitization of stainless steel AISI 304L, AISI 316L, AISI 321 and AISI 347 pipes used in petroleum refining plants. The sensitization was assessed by Scanning Electron Microscopy (SEM) according to ASTM A-262 and by the Double Loop Electrochemical Potentiokinetic Reactivation test (DLEPR). The results showed that all steels did not present sensitization at operating temperature (380°C) in the desulfurizers process, but the temperature of 500°C was critical to the appearing of sensitization for the both low carbon stainless steels and AISI 321 SS, while for the AISI 347 the critical temperature was 550°C. The stabilized steels confirmed to be more resistant to sensitization than the low carbon stainless steels, and niobium showed to be more efficient stabilizing agent than titanium.


## 1. Introduction

Sensitization is a deleterious phenomenon that occurs in austenitic stainless steel (SS) when it is submitted to an inappropriate increase in temperature such as what happens during welding or operating in the temperature range between 400°C and 800°C. This is a well-known phenomenon and consists of carbide precipitation at grain boundaries and chromium depletion in adjacent regions, making the material susceptible to intergranular corrosion [1]. Recently, a previous study from our laboratory showed that sensitization at 650°C also promotes the embrittlement of the AISI 304 steel [2].

The AISI 321 SS has been used in the desulfurizing process in the petroleum refining plants because of its good corrosion resistance and mechanical properties at the operating temperature of 380°C. However, despite the fact that this steel contains titanium in order to combine with carbon to avoid chromium carbide precipitation, a practical case previously studied [3] showed that AISI 321 SS tubes were unsuitable after one year of operation due to severe sensitization. This occurrence was related to the increase of the temperature, which reaches around 600°C during shutdown for maintenance or power failure. This practical case is in accordance with Padilha *et al.* [4], which showed that at temperatures around 600°C chromium carbide formation was more favorable than titanium carbides.

Additionally, it is shown in the literature [5–7] that it is possible to nucleate carbides on grain boundaries by brief exposure of the SS at temperatures in the normal sensitization range without observation of a detrimental degree of chromium depletion. However, sensitization can develop during subsequent heat treatment at low temperature which is not expected to cause sensitization. This phenomenon has been termed as low-temperature sensitization (LTS). Thus, this practical observation of the AISI 321 SS tubes can be explained by the temperature excursions to 600°C resulting in the formation of the carbide nuclei that were then stable enough to grow at very low temperature (380°C).

Since the studied case showed that sensitization was not avoided even using a titanium stabilized AISI 321 SS [3], it is suitable to study alternatives SS to be used in a petroleum refining plant. Thus, this work carried out a systematic investigation of the influence of time on the intergranular corrosion of the AISI 304L, AISI 316L and AISI 347 steels with the temperature range varying from the operational temperature of 380°C

*Author to whom all correspondence should be addressed.

TABLE I Chemical compositions of austenitic stainless tubes in wt%

| Steel/elements | Cr (%) | Mn (%) | P (%) | Si (%) | Ni (%) | Mo (%) | Ti (%) | Nb (%) | C (%) |
|---|---|---|---|---|---|---|---|---|---|
| AISI 304L | 17.2 | 1.68 | 0.012 | 0.245 | 10.8 | – | – | – | 0.03 |
| AISI 316L | 18.3 | 1.54 | 0.012 | 0.622 | 9.8 | 0.423 | – | – | 0.03 |
| AISI 321 | 14.1 | 2.81 | 0.037 | 0.957 | 15.2 | – | 0.818 | – | 0.08 |
| AISI 347 | 18.9 | 1.37 | 0.017 | 0.308 | 9.79 | – | – | 0.841 | 0.08 |

up to 600°C. The AISI 321 tubes were also studied at the same conditions for comparison. The AISI 304L and AISI 316L were chosen because they are less expensive than AISI 321 and contain low carbon percentage (≤0.3 wt%) to minimize the sensitization when operating in this temperature range, while AISI 347 was chosen to be another stabilized steel containing niobium to combine with carbon to avoid sensitization. The evaluation of the sensitization at the different heat treatment conditions was assessed by optical microscopy and scanning electron microscopy techniques and double loop electrochemical potentiokinectic reactivation test (DLEPR), proposed by Akashi *et al.* [8].

## 2. Experimental

### 2.1. Materials and samples preparation

Four austenitic stainless types ASTM A 312, 2.5 in diameter tube, with the chemical composition shown in Table I, were used in this investigation. Samples with approximately 1 $cm^2$ of quadrangular geometric face were obtained from each tube, as shown in Fig. 1. The samples were heat treated at different temperatures and different periods of time as shown in Fig. 3. All the samples were put at the same time in a preheated air furnace atmosphere, at the desired temperature, and after each period of time they were cooled in water. One of them was picked up for metallographic preparation and two other for electrochemical test. The others returned to the furnace and stayed there until the new period of time has being reached. This operation was systematically repeated until 96 h. A total of 424 samples, 105 of each steel and four in the condition as received, were prepared. The objective of this sequence was to simulate a long period of operation with many shutdowns.

### 2.2. Metallographic etchings

Metallographic etching according to ASTM A-262 was performed. Photomicrographs were acquired using a Zeiss optical microscope and a Philips XL-30 scanning electron microscope (SEM). The microstructures obtained were classified into three types: "step" structure with no ditches at grain boundaries; "dual" structure, with some ditches at grain boundaries; and, "ditch" structure, with one or more grains completely surrounded by ditches. Fig. 2 presents the microstructures classified according ASTM A-262.

### 2.3. DLEPR tests

The DLEPR tests were conducted in a conventional three-electrode cell using a Pt foil as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference one. The working electrode was constructed using SS samples embedded in epoxy resin. The experiments were initiated after nearly steady-state open circuit potential ($E_{oc}$) had developed (about 30 min)

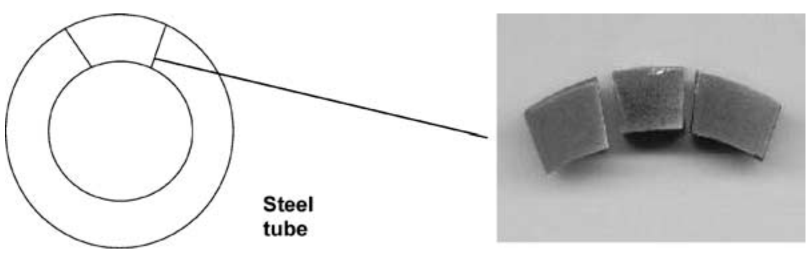


*Figure 1* Geometry of samples obtained from the tubes.

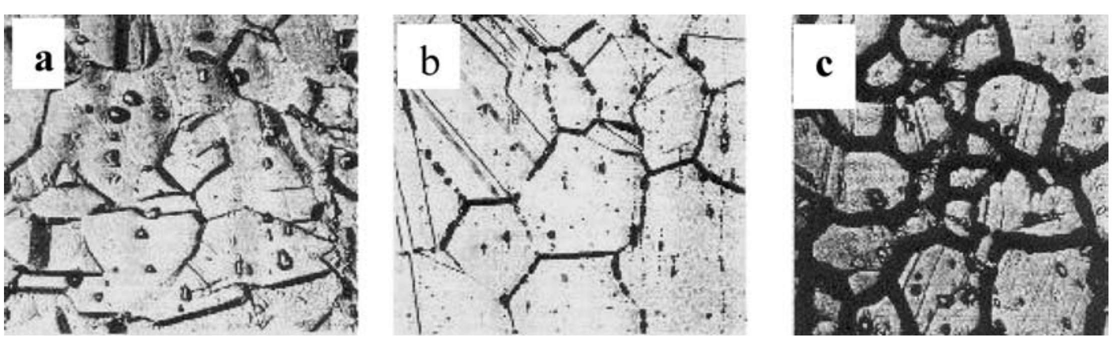


*Figure 2* Classification of sensitized microstructure according to ASTM A-262: (a) step, (b) dual, and (c) ditch.

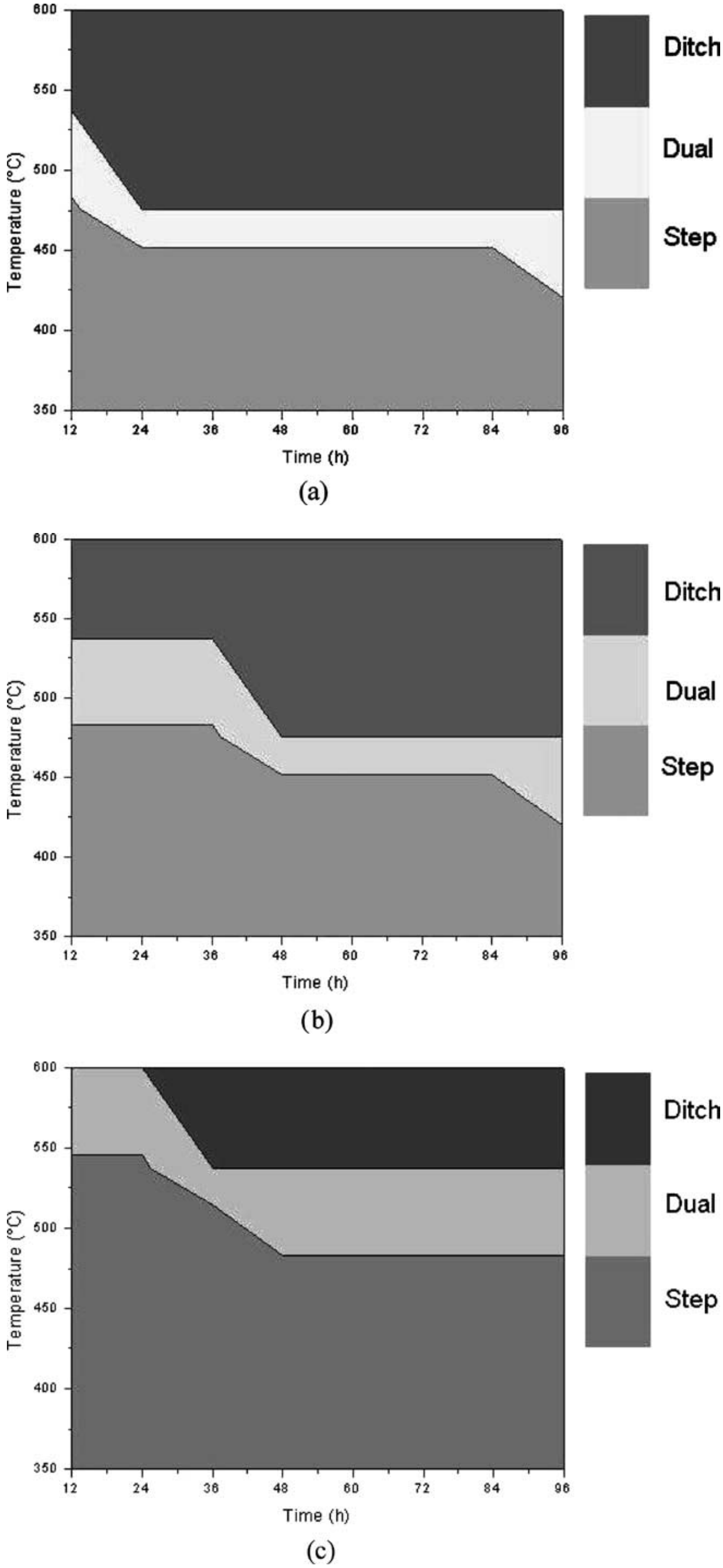


*Figure 3* Classification of the microstructures observed on samples of AISI 304L and AISI 316L (a), AISI 321 (b) and AISI 347 (c) for different time of exposition to temperature range from 380 to 600°C according ASTM A-262.

followed by the potential sweep in the anodic direction at 1 mV $s^{-1}$ until the potential of 0.3 V (vs. SCE) was reached, then the scan was reversed in the cathodic direction until the $E_{oc}$. Prior to each experiment, the working electrodes were polished with 400 grit emery paper, degreased with alcohol and cleaning in water. The working solution was 0.5 M $H_2SO_4$ + 0.01 M KSCN (potassium thiocyanate). The sensitization intensity was evaluated from the ratio $I_r/I_a$, where $I_a$ is the peak current of the anodic scan and $I_r$ is the peak current in the reversed scan [1, 8].

## 3. Results and discussion

The plots shown in Fig. 3 present the classification of microstructure of the SS samples after exposure to temperature from 380 to 600°C and periods of time from 0 to 96 h. The microstructures were

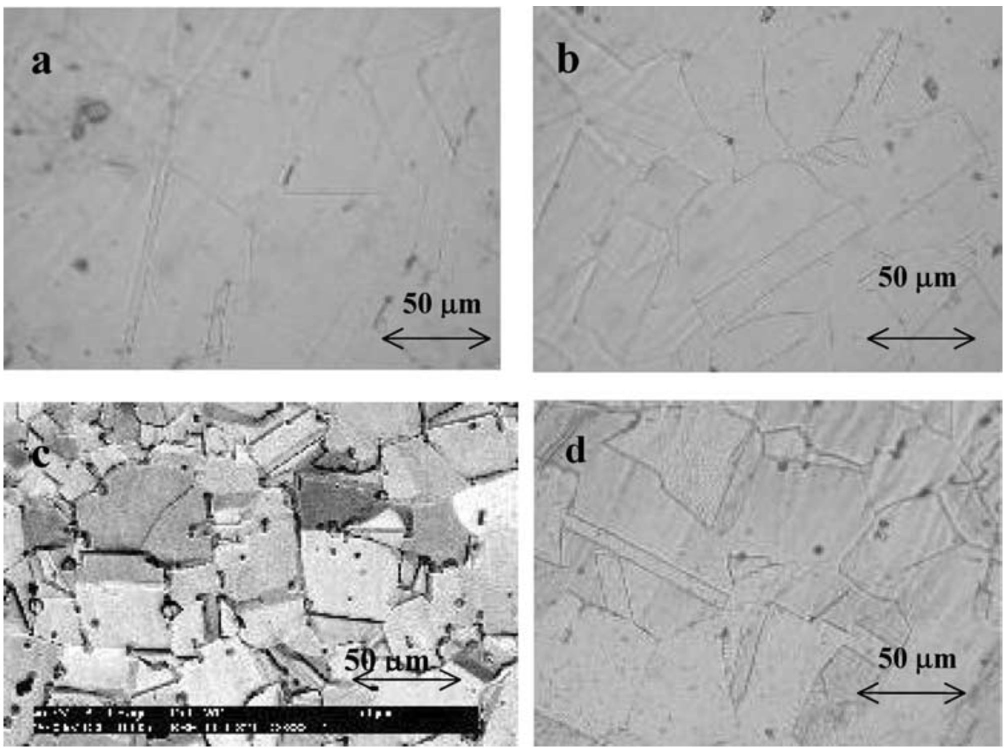


*Figure 4* Microstructures of AISI 304L SS (a), AISI 316L SS (b), AISI 321 SS (c) and AISI 347 SS (d) samples exposed 96 h at 380°C.

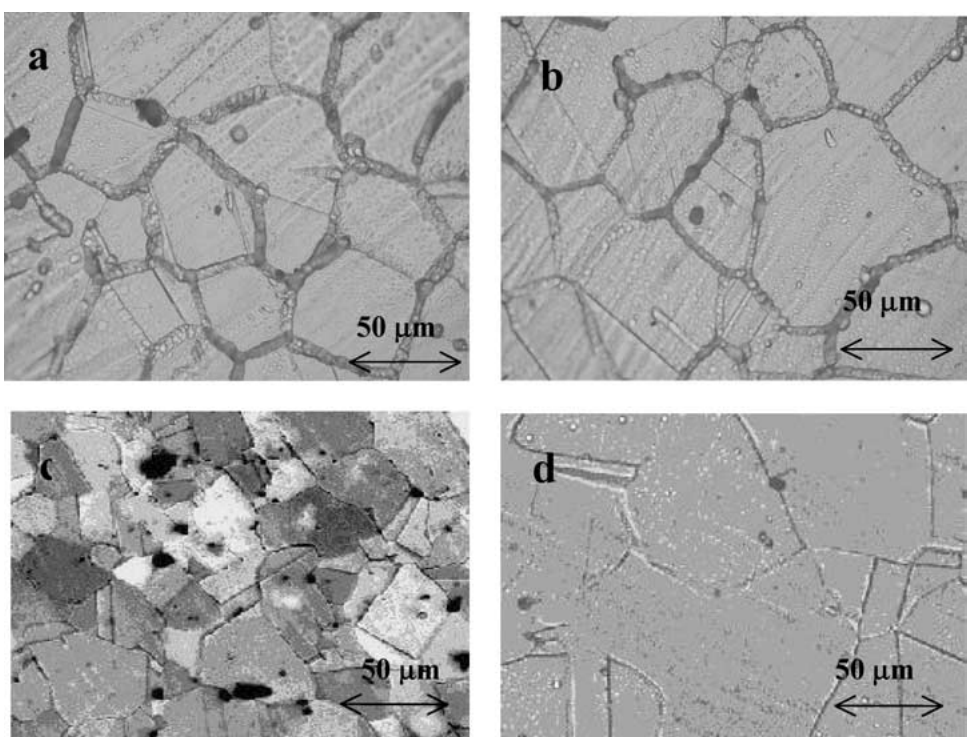


*Figure 5* Microstructures of AISI 304L SS (a), AISI 316L SS (b), AISI 321 SS (c) and AISI 347 SS (d) exposed 24 h at 500°C.

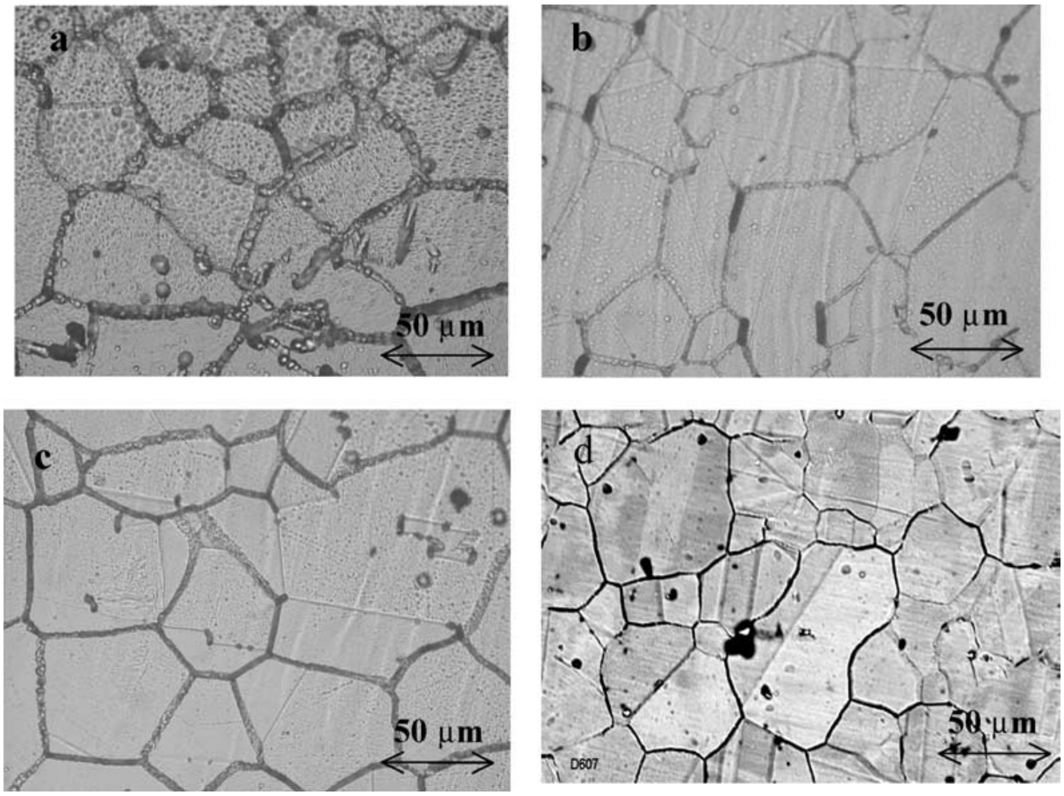


*Figure 6* Microstructures of AISI 304L SS (a), AISI 316L SS (b), AISI 321 SS (c) and AISI 347 SS (d) exposed 24 h at 600°C.

classified according to ASTM A-262 standard, as shown in Fig. 1.

A very important practical result is revealed by these plots. All the four steels did not show a sign of sensitization at 380°C, the operational temperature in the desulfurizers process in petroleum refining plants, suggesting that all are suitable to be used for this application if the temperature is maintained under control at 380°C. Fig. 4 shows the microstructures for samples of the four steels which were exposed to 380°C for 96 h.

These plots also reveal that at 450°C the dual microstructure is only observed in samples of AISI 304L, AISI 316L and AISI 321 heat treated for 96 h. Additionally, it can also be observed in Fig. 3 that at 500°C the sensitization process is evident, even in short exposure time, and the microstructure of the samples exposed at 500°C during 24 h is shown in Fig. 5. The micrographs of AISI 304L (Fig. 5a) and AISI 316L (Fig. 5b) samples show microstructure classified as ditch, indicating that these materials were sensitized. The micrograph of AISI 321 (Fig. 5c) sample presents some chromium carbides around grains characterizing a dual microstructure, while the micrograph of AISI 347 (Fig. 5d) sample presents a chromium carbide free structure characterizing a step structure. On the other hand, all the steel samples presented ditch structures when heat treated at 600°C after 24 h in the furnace, as can be observed in Fig. 6. According to these analyses, the stabilized steels are more resistant to sensitization than the low carbon steels. Additionally, these results also suggest that niobium is more efficient than titanium to avoid sensitization, since ditch structure was observed for AISI 347 SS samples only when this material was heat treated at 550°C after 48 h (see Fig. 3c).

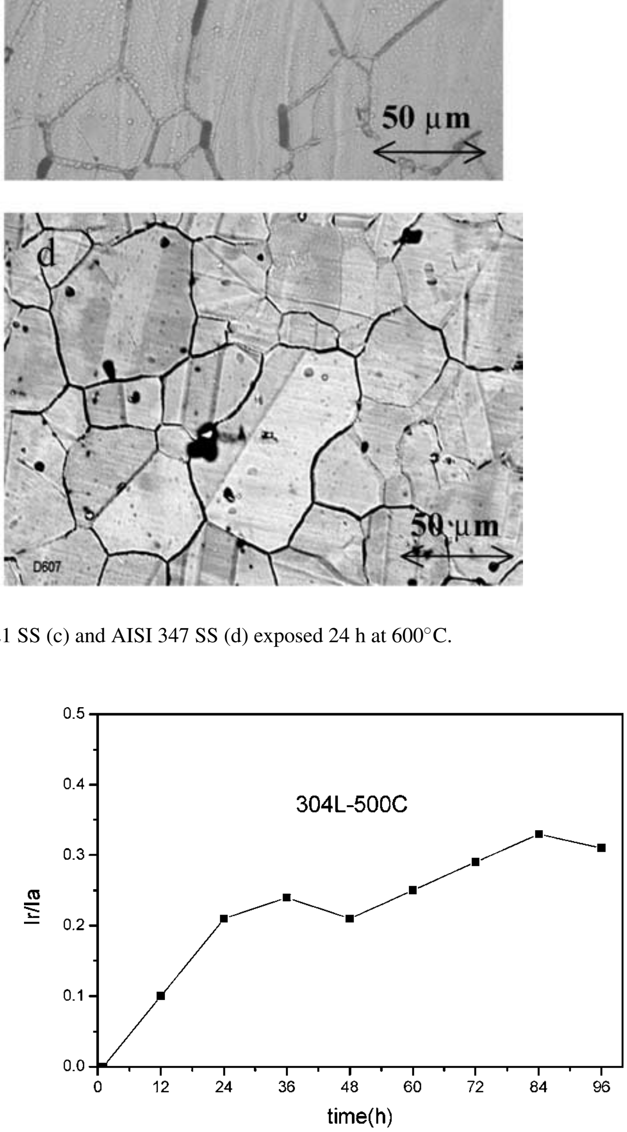


*Figure 7* The sensitivity intensity evaluated from the ratio of $I_r/I_a$ for AISI 304L at 500°C.

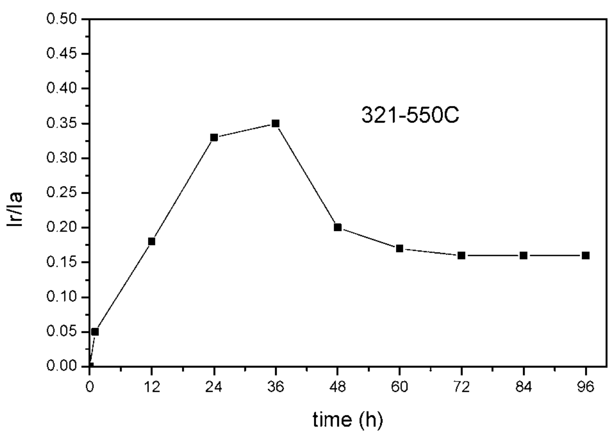


*Figure 8* The sensitivity intensity evaluated from the ratio of $I_r/I_a$ for AISI 321 at 550°C.

TABLE II Time of heat treatment to reach the maximum of $I_r/I_a$

| Steel/T (°C) | 380° | 450° | 500° | 550° | 600° |
|---|---|---|---|---|---|
| AISI 304L | 96 h | 96 h | 84 h | 24 h | 84 h |
| AISI 316L | 96 h | 96 h | 36 h | 84 h | 84 h |
| AISI 321 | 36 h | 48 h | 84 h | 36 h | 24 h |
| AISI 347 | | | | 130 h | |

Figs 7 and 8 show the sensitization intensity evaluated from the electrochemical tests through the ratio of $I_r/I_a$, where $I_a$ is the peak current of the anodic scan and $I_r$ is the peak current in the reverse scan, for a AISI 304L sample at 500°C and a AISI 321 sample at 550°C, respectively. For each temperature and steel a maximum value of the ratio $I_r/I_a$ has been obtained. Table II shows the temperature and time of exposure in which the maximum value of $I_r/I_a$ is reached. Observe that for samples of AISI 304L, 316L and 321 the maximum value is at 500°C and for AISI 347 is at 550°C.

## 4. Conclusions

The main conclusions of this work are:

- All the studied steel did not present sensitization when submitted to heat treatment at operating temperature (380°C), but the temperature of 500°C is critical to the appearing of sensitization for the both low carbon steel and AISI 321 SS, while for the AISI 347 the critical temperature is 550°C.
- The addition of niobium and titanium to steel composition is more efficient to reduce the sensitization than the decrease of the carbon content in steel composition.
- Niobium is a more efficient stabilizing agent than titanium for this study conditions.


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