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Effects of solution heat treatment on grain growth and degree of sensitization of AISI 321 austenitic stainless steel

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This work investigates the influence of solution temperature on grain growth and degree of sensitization of AISI 321 steel. Samples were solution treated at temperatures between 800 and 1,200°C for 80 min and sensitized at 600°C for 105 h. Optical microscopy and double loop electrochemical potentiodynamic reactivation (DLEPR) techniques were used to characterize and evaluate the degree of sensitization. The grain coarsening temperature (T_{gc}) found was 1,080°C, with occurrence of abnormal or discontinuous grain growth. Samples submitted to solution heat treatment below 1,080°C presented average grain diameter approximately equal to those presented by non-heat treated samples. The sensitization process at 600°C for 105 h became null when the samples were previously solution treated at 800 or 900°C, for 80 min. Sensitized and previously solution treated samples for temperatures greater than 1,075°C presented a decrease in sensitization intensity and an increase in transgranular precipitation.

1. Introduction

Austenitic stainless steels (SS) present high resistance to corrosion under various aggressive environments and therefore are widely used in different areas, especially in industry. However, such material can be sensitized during welding, during the slow cooling process after solution heat treatment or even during the stress relief in the temperature interval of chromium carbide precipitation. Sensitization consists of chromium carbide precipitation, particularly $Cr_{23}C_6$, in the grain boundaries, producing a depletion of chromium atoms in regions adjacent to the boundaries. Sensitized steels can be subject to intergranular corrosion (IGC) [1], a fact that may affect their behavior in future applications.

One way of avoiding sensitization, and consequently IGC, is the addition of elements that strongly induce the formation of carbides in the base-steel, such as titanium and niobium, which present greater affinity to carbon, in contrast to chromium. AISI 321 austenitic SS has titanium as its stabilizing element, which on combining

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with carbon strongly reduces the amount of carbon available in the matrix to form chromium carbides. Another way to prevent the sensitization of austenitic SS consists in solution heat treatment by increasing the steel temperature above the solvus chromium carbide line, for a specified hold period. After the total or partial chromium carbide dissolution, a quick cooling is applied to avoid reprecipitation.

The grain coarsening temperature (T_{gc}) is defined as being the temperature at which abnormal or discontinuous grain growth occurs during the solution heat treatment of microalloyed steels. Grain growth at temperatures below the T_{gc} undergoes a slight increase due to the pinning of the grain boundaries by fine carbide particles [2]. For solution temperatures between the T_{gc} and the temperature at which these particles are completely in solution (T_s), due to Ostwald ripening and the dissolution, the average particle diameter surpasses a critical value, generating abnormal grain growth or secondary recrystallization [3].

Since chromium carbide dissolution is slow during the solution heat treatment, it is necessary to find a solution temperature high enough to dissolve more chromium carbides but at the same time lower than the T_{gc}, in order to avoid the formation of a highly heterogeneous microstructure. In the case of AISI 321 austenitic SS, high solution temperatures must also be avoided due to the higher carbon concentration released by the dissolution of titanium carbides.

AISI 321 austenitic SS tubes used in the desulfurization processes in petroleum refineries, have shown, after a year, that at temperatures between 350°C and 380°C, they may present typical intergranular stress corrosion cracking (SCS) [4]. This was caused by severe sensitization of the steel by occasional increases in the temperature, up to 600°C, during the few hours of shutdown for plant maintenance or in the event of power failures.

In the present work, the effects of solution heat treatment on the grain growth behavior and in the degree of sensitization of an AISI 321 austenitic SS tube, used in petroleum refineries, were investigated by optical microscopy and double loop electrochemical potentiodynamic reactivation tests (DLEPR) [5]. The aim of the work was to establish optimal conditions to use under wide variations of operational temperatures.

2. Experimental

2.1. Material and sample preparations

An austenitic SS type ASTM A312 TP321 tube (6.35 cm in diameter) with chemical composition shown in Table I was used in the present work. The chemical characterization was carried out with a Link Analytical QX-2000 X-ray dispersive energy analyzer (EDX) attached to a SEM apparatus. In order to obtain samples with observation faces typical of the internal tube surface, quadrangular samples (1.0 cm^2 of geometrical area) were cut from the tube. The samples not submitted to thermal treatment were labeled "as-received" samples (AR).

TABLE I Chemical composition (weight%) of the ASTM A312 TP321

Elements	C	Mn	Si	Ni	Ti	Cr
wt%	0.05	1.823	0.688	7.546	0.473	17.42

To investigate the grain growth behavior as a function of the solution temperature, AR samples were treated in a pre-heated furnace at different temperatures, between 800 and 1,200°C, for 80 min under air atmosphere, and then followed by water quenching. These samples were labeled "solubilized" samples (SO).

In order to simulate AISI 321 austenitic SS sensitization caused by extensive operation intervals under occasional temperature peaks [4], a "sensitized" sample (SE) was prepared from AR sample thermally treated at 600°C for 105 h. At time intervals of 1, 10 and 50 h, the sample was removed from the furnace, quenched in water and returned back to the furnace. After completing 105 h, a final sample quenching was performed.

To study the effects of the solution heat treatment on the sensitization along extensive time intervals, SO samples were put at 600°C for 105 h, followed by water quenching, and labeled as "sensitized and solubilized" samples (SSS).

2.2. Metallographic etchings

Qualitative analyses of the degree of sensitization on the AR, SE and SSS samples submitted to different conditions of thermal treatments were made by metallographic examinations and according to ASTM A262–Practice A [6]. The microstructures that showed no ditches on all grain boundaries were classified as "step" structures; the ones that showed some ditches at grain boundaries, in addition to the steps but no single grain completely surrounded by ditches, as "dual" structures, and with one or more grains completely surrounded by ditches as "ditch" structures.

To examine grain boundaries without the interference of annealing twin, the AR and SO samples were etched in a solution prepared by diluting concentrated nitric acid in water 50% v/v and the average grain diameter measured with an image analysis system, which included an Olympus BX51 optical microscope.

2.3. Double loop electrochemical potentiodynamic reactivation tests (DLEPR)

In order to evaluate quantitatively the susceptibility of the AISI 321 steel to intergranular attack, DLEPR tests were performed at room temperature (~25°C) in a conventional three-electrode electrochemical cell with Pt foil as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrolytic solution was 0.05 M H_2SO_4 + 0.01M KSCN. The working electrode was constructed with the AISI 321 samples embedded in polyester resin. After reaching the nearly

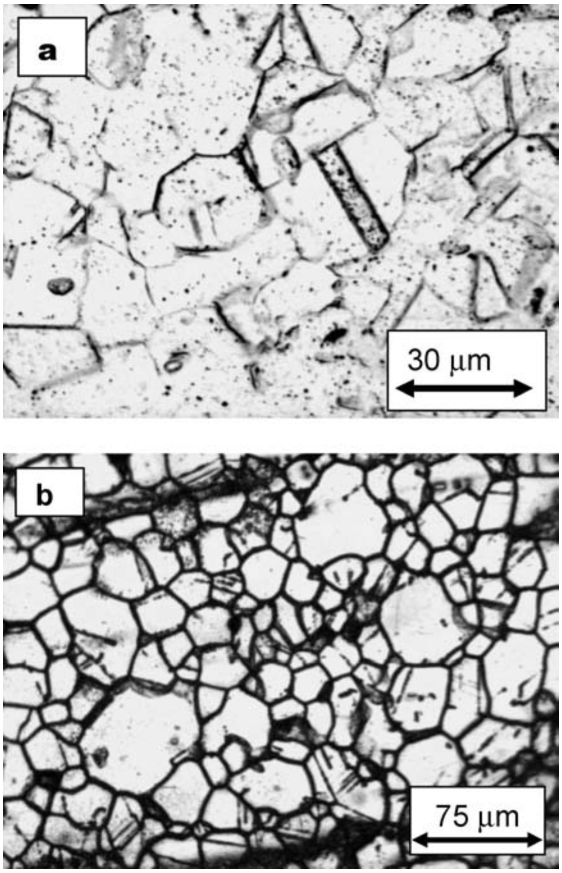

Figure 1 Micrographs of the AR sample: (a) "step" structure (according to ASTM A262—Practice A) and (b) grain boundaries (electrolytic etching in 50% nitric acid solution).

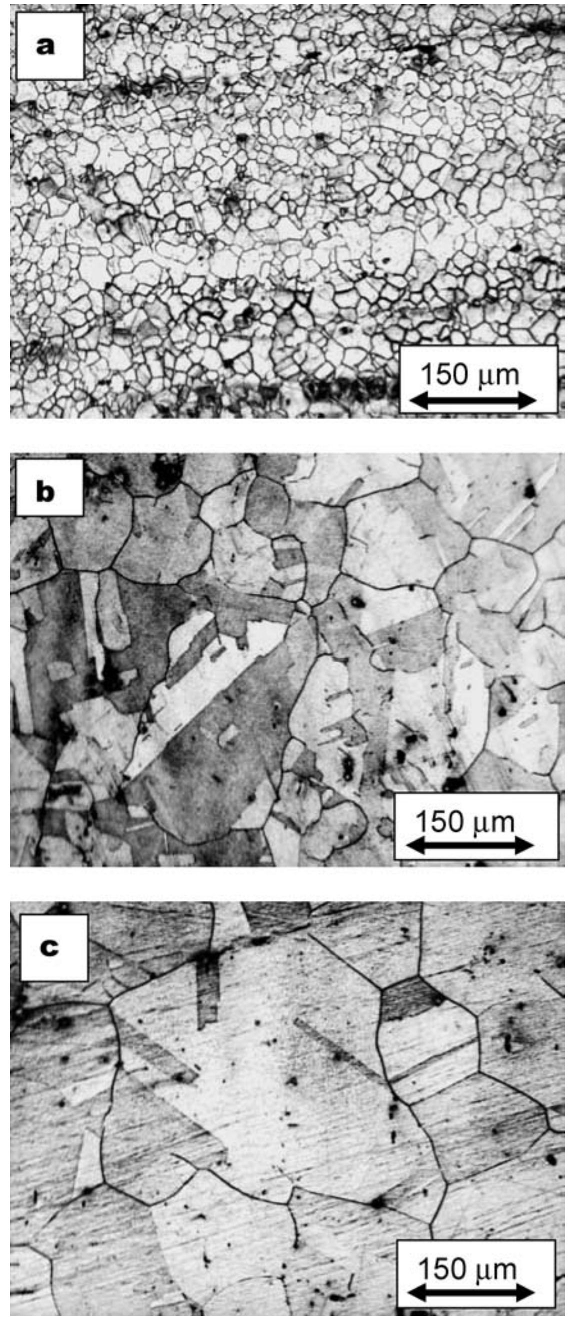

Figure 2 Micrographs of SO samples heat treated at (a) 1,000°C, (b) 1,150°C and (c) 1,200°C; for 80 min.

steady-state open circuit potential (E_{oc}) (about 30 min), the potential was swept in the anodic direction up to 0.6 V at 1 mVs^{-1} and then scanned back to the E_{oc}. The degree of sensitization (or the sensitization intensity) was evaluated from the I_r/I_a ratio, where I_a and I_r represent the anodic and reversed peak currents [5].

3. Results and discussion

The microstructure of an AR sample etched according to the ASTM A262 —Practice A (Fig. 1a) shows a "step" microstructure. On the other hand, after electrolytic etching in the nitric acid solution (Fig. 1b), the surface reveals a relative homogeneous grain distribution. The average grain diameter and the sensitization intensity (I_r/I_a) for the AR sample were calculated as 18 μm and 0.014, respectively. The presence of some grains larger than the average value in Fig. 1b indicates that microstructures with secondary recrystallization may be developed after further thermal treatment.

A study of grain growth behavior as a function of the solution temperature was conducted for a better understanding of the phenomena occurring in the material during the solution heat treatment. At temperatures below 1,080°C, the microstructure appeared relatively homogeneous, with the average grain diameter remaining practically constant, close to 18 μm (Fig. 2a). At temperatures equal or higher than 1,080°C, the grain growth increased rapidly (Fig. 2b and c). At 1,080°C the emergence of secondary recrystallization can be noted, marking a change in the grain growth behavior.

The dependence of the average grain diameter on the solution temperature is shown in Fig. 3 and the values given in Table II. This figure presents characteristics that clearly confirm what was already observed in the micrographs of the SO samples.

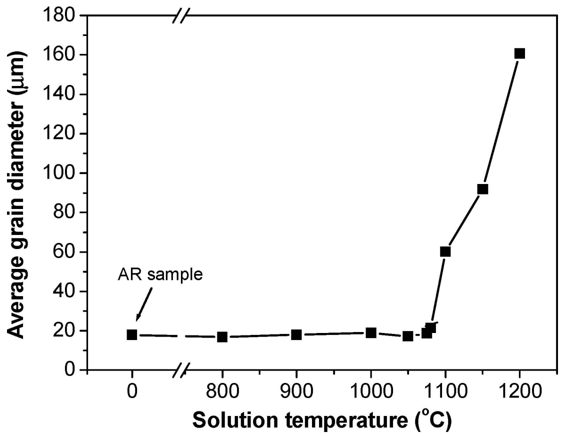

Figure 3 Grain growth behavior as a function of the solution temperature.

TABLE II Average grain diameter and sensitization intensity for different heat treatment temperatures of the ASTM A312 TP321

Heat treatment	Temperature (°C)	Average grain size (μm)	Sensitization intensity
As received	–	18±1	0.014
Sensitization	600	–	0.628
Solution	800	17±2	0.019
	900	18±2	0.017
	1000	19±4	0.160
	1050	17±2	0.418
	1075	19±1	0.582
	1080	21±2	–
	1100	60±14	0.356
	1150	92±14	0.460
	1200	160±26	0.319

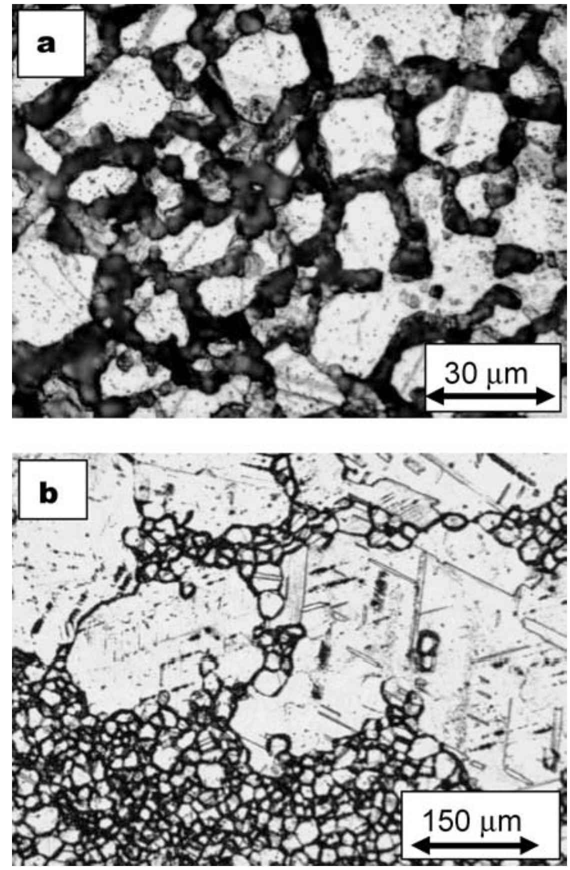

Figure 4 Micrographs of SE sample heat treated at 600°C for 105 h showing (a) "ditch" structure and (b) secondary recrystallization.

Figs 2a and 3 show that, at temperatures below 1,080°C, the grain growth is strongly inhibited by titanium carbide particles, which keep the average grain diameter close to 18 μm. This grain growth behavior indicates that, at this temperature interval, these particles are practically insoluble. At 1,080°C, determined as the T_{gc}, occurs the abrupt change in the grain growth behavior (Fig. 3), caused by the appearance of secondary recrystallization. This temperature is lower than the 1,271.44°C, estimated as the T_s of TiC for AISI 321 austenitic SS based on Ref. [7]. According to Cuddy *et al.* [8], who observed the same result for lower carbon microalloyed steels, to free the grain boundaries the particles should dissolve and grow only to the extent that the pinning force falls below a critical value. At 1,080°C and higher temperatures, the amount of carbon in the solution matrix increases progressively until dissolution of all particles.

The microstructure of the SE sample revealed strong chromium carbide precipitation in the grain boundaries (Fig. 4a) and also the presence of secondary recrystallization (Fig. 4b). According to the ASTM A 262— Practice A, such microstructure can be classified as "ditch". Furthermore, the sensitization intensity (I_r/I_a) for this sample was calculated as 0.628.

The presence of secondary recrystallization in Fig. 4b can be attributed to chromium carbide particles ripening during the sensitization thermal treatment, since it is well known that keeping steels that contain precipitated particles at a fixed temperature, below solvus line, causes particle ripening. Furthermore, ripening of titanium carbide particle is meaningless, even at high temperatures, due to its low solubility in the austenite [9].

The microstructures of the SSS samples for solution temperatures of 800 and 900°C presented a "step" shape, as illustrated in Fig. 5a for 900°C. At and above 1,000°C, a "ditch" shape was observed (Fig. 5b and c). Similar results were reported by Silva *et al.* [4] in a study where 900°C solution temperature was determined as the best option to prevent sensitization at 600°C. These authors claimed that the higher the solution temperature the higher the sensitization intensity, as a consequence of titanium carbide dissolution with the increase of the solution temperature. In a sensitization thermal treatment, after solution treatment, the carbon atoms may bind to chromium atoms forming chromium carbides, since at temperatures of about 600°C, the kinetic of chromium carbide formation is strongly favored rather than titanium carbide [10].

In the SSS samples submitted to solution temperatures equal or higher than 1,050°C (Fig. 5c),

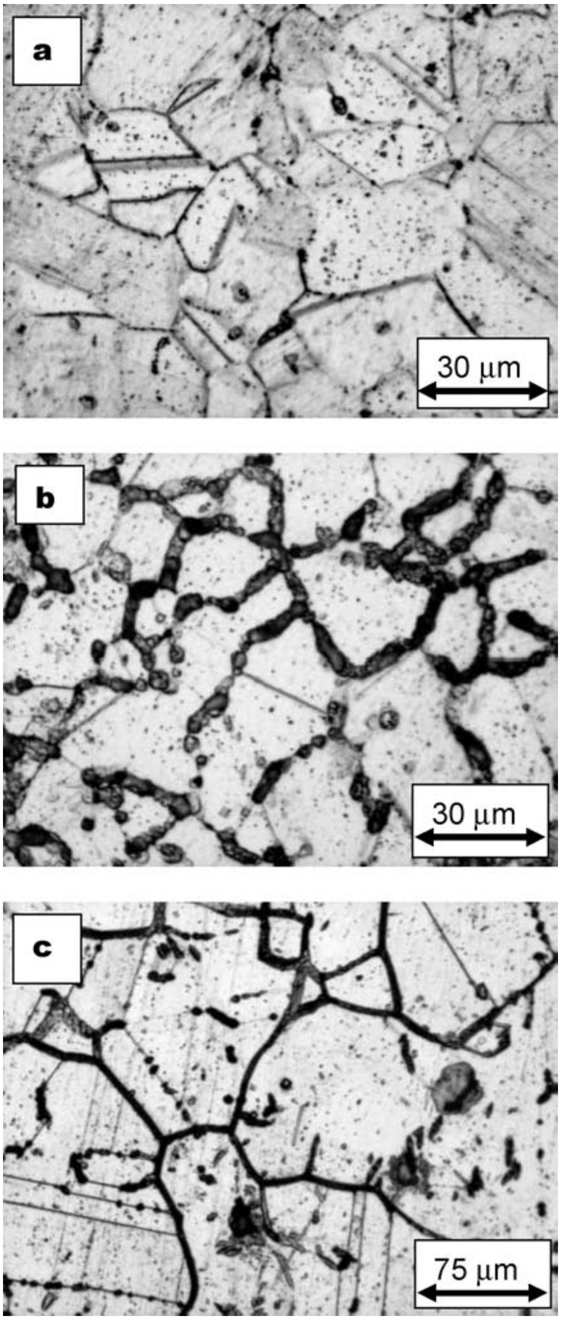

Figure 5 Micrographs of SSS samples previously solution treated at (a) 900°C, (b) 1,000°C, and (**c**) 1,150°C; for 80 min, right after sensitization at 600°C for 105 h.

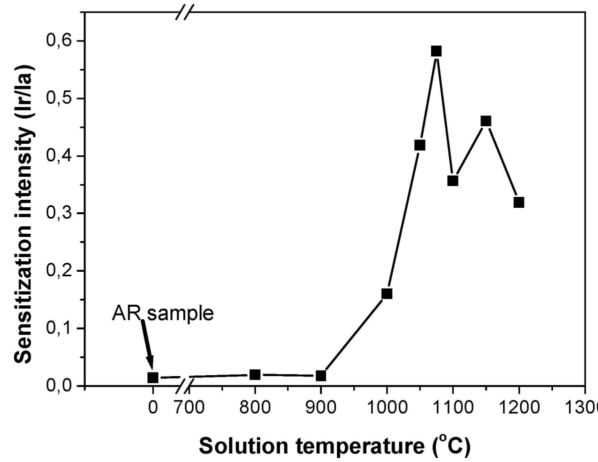

Figure 6 Variation of the degree of sensitization for SSS samples previously solution treated at different temperatures, for 80 min and right after sensitized at 600°C for 105 h.

transgranular precipitation was observed. Such precipitation occurs within the grains, particularly at high supersaturation, mainly in preferential sites such as dislocations and solute atom/vacancy clusters [11].

For the SSS samples, the intergranular sensitization intensity behavior as a function of the solution temperature (Fig. 6 and Table II) was evaluated from the electrochemical tests. It can be noted that at temperatures of 800 and 900°C, the I_r/I_a remains practically equal to the one found in the AR sample. Above 900°C, the sensitization intensity increases rapidly, reaching a maximum value at 1,075°C and then followed by a gradual decrease.

With respect to the identification of the solution heat treatment effects over the degree of sensitization of the material at 600°C for 105 h, Fig. 6 clearly shows that solution temperatures of 800 and 900°C efficiently prevent the sensitization. Nevertheless, between 1,000 and 1,075°C, an increase in the sensitization intensity occurs with the solution temperature, probably motivated by the increase of chromium and carbon diffusion during the solution treatment. The larger the amount of solute caused by the increase in the solution temperature, the higher the nucleation rate and the chromium carbide growth during the sensitization treatment. At solution temperatures higher than 1,075°C, a decrease in the intergranular sensitization intensity takes place. This effect can also be verified in the micrographs in Fig. 5, since the boundary width remains practically the same and the grain boundary area per unit volume decreases from T_{gc}. In this stage, precipitation is reinforced due to an increase in the amount of carbon in solution supplied by the titanium carbide dissolution. Although the transgranular precipitation is already present at 1,050°C, due to the supersaturation phenomenon, it will surpass the intergranular precipitation only after the matrix receives supplementary amounts of carbon in solution.

4. Conclusions

From the present study, it may be concluded that:

(i) The grain coarsening temperature for solution heat treated AISI 321 austenitic SS, for 80 min, was determined as 1,080°C and below this temperature the titanium carbide particles in the matrix remained inert;

(ii) The appearance of secondary recrystallization in the microstructure of the AISI 321 austenitic SS sensitized at 600°C, for 105 h, was attributed to chromium carbide particles ripening during the sensitization treatment;

(ii) It has been demonstrated that solution temperatures of 800 and 900°C were efficient to prevent sensitization of AISI 321 SS heat treated at 600°C for 105 h;

(iv) The intergranular sensitization intensity as a function of the solution temperature, reaches a maximum around 1,075°C and then decreases immediately after, probably due to an increase in the transgranular precipitation.

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