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Influence of stabilization heat treatments on microstructure, hardness and intergranular corrosion resistance of the AISI 321 stainless steel

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Abstract The AISI 321 is an austenitic stainless steel which contains Ti as stabilizing element. This material can be selected for high temperatures services due to its high creep and intergranular corrosion resistance. However, for services into the sensitization range of temperatures (450–850 °C), the steel must be previously heat treated at higher temperatures for TiC precipitation. In the present work the importance of this so-called stabilization treatment, and the best range of temperatures for its realization, were investigated by means of microscopy and electrochemical potendynamic reactivation tests. It was found that the higher temperature for stabilization must be 950 °C. Samples stabilized at 975 °C or 1000 °C and aged at 600 °C for 100 h showed the very begin of the sensitization process.

Introduction

Stabilized austenitic stainless steels such as AISI 321 and 347 may be suitable for high temperatures applications, due to the creep resistance of the fcc austenitic structure. The intergranular TiC and NbC fine precipitation has double function: they prevent sensitization and intergranular corrosion and also improve the creep resistance of the steel.

However, the stabilized austenitic steels must be heat treated at high temperatures before use at 600–800 °C. The objective of this so called stabilization treatment is to promote the precipitation of all carbon present in the steel as TiC (or NbC) carbides and preserve chromium in solid solution during the high temperature service. According to Min et al. [1], TiC carbides promote longer creep-fatigue life than $Cr_{23}C_6$ carbides. The ASTM A358/358M standard [2] states that the temperature of the stabilization treatment must be mutually agreed on by the customer and the manufacturer.

The focus of the present work was to evaluate the importance of the stabilization heat treatment on the ntergranular corrosion resistance of the AISI 321 steel subjected to long periods of aging at 600 °C. Five stabilization temperatures in the 850 °C to 1025 °C range were tested in order to find the best temperature range. The effect of the stabilization treatment on the hardness was also determined.

Experimental

The AISI 321 steel studied in this work was purchased in solution treated condition (1100 °C, water quenched). The chemical composition is shown in Table 1. Samples were cut from the plate and heat treated in air at 850 °C, 875 °C, 900 °C, 950 °C and 975 °C, 1000 °C and 1025 °C for 2 h, followed by air cooling. After these stabilization treatments the samples were aged at 600 °C for selected times up to 100 h. The microstructures were observed in optical and scanning electron microscopes. The samples were

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Table 1 Chemical composition of the steel (wt%.)

C	Si	Mn	P	S	Cr	Ni	Ti	N
0.035	0.41	1.50	0.024	0.009	17.16	9.08	0.380	0.016

electrolytically etched in oxalic acid solution, as described in the ASTM A262 standard (practice A) [3].

The intergranular corrosion resistance was investigated by double loop electrochemical potentiodynamic tests (EPR-DL) [4]. These 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 the AISI 321 samples embedded in epoxy resin. The tests were initiated after nearly steady-state open circuit potential (E_{oc}) had developed (about 30 min) followed by the potential sweep in the anodic direction at 1 mV s^{-1} until the potential of 0.35 V_{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 grid 400 emery paper, degreased with alcohol and cleaned in water. The electrolyte was 0.5 M H_2SO_4 + 0.01 M KSCN solution. The degree of sensitization was evaluated by 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.

Vickers hardness tests with 30 kgf load (HV30) were carried in all stabilized conditions.

Results and discussion

Figure 1 shows the microstructure of the sample in the solution treated condition. This is a ''step'' microstructure [3], containing coarse and square shaped TiN particles (indicated by arrows). Figure 2 shows the sample which was aged at 600 °C for 24 h without previous stabilization.

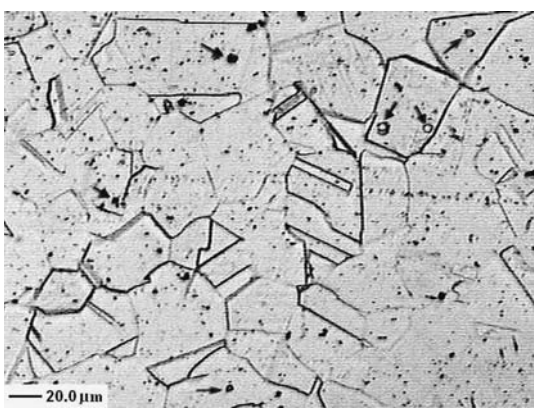

Fig. 1 Solution treated sample. TiN particles are indicated by arrows

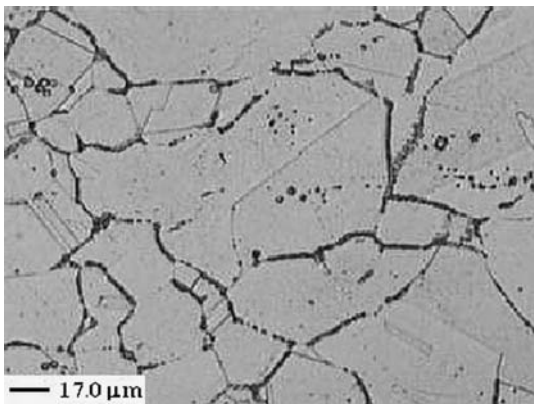

Fig. 2 Sample aged at 600 °C for 24 h without previous stabilization treatment

The interganular carbides precipitation is revealed by the electrolytic etch in 10% acid oxalic solution. The EPR-DL curve at this condition (Fig. 3) shows an I_r/I_a = 0.17, typical of sensitized material [3]. Figure 4 shows the sample just after the EPR-DL test, with the intergranular attack. This experience shows that the AISI 321 steel in the solution treated condition undergoes sensitization at high temperatures, in a similar manner as other non stabilized steels.

Figure 5 shows the microstructure of the sample aged at 600 °C for 100 h with previous stabilization at 875 °C. Figure 6a and b shows the microstructures of samples stabilized at 950 °C and aged at 600 °C for 24 h and 100 h,

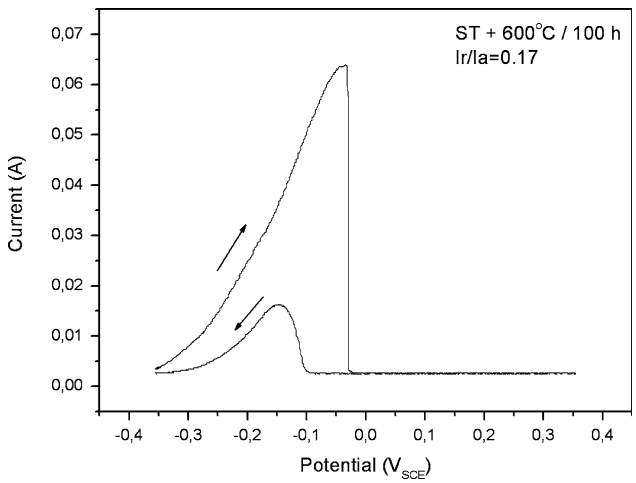

Fig. 3 EPR-DL curve of the sample aged at 600 °C for 24 h without previous stabilization treatment

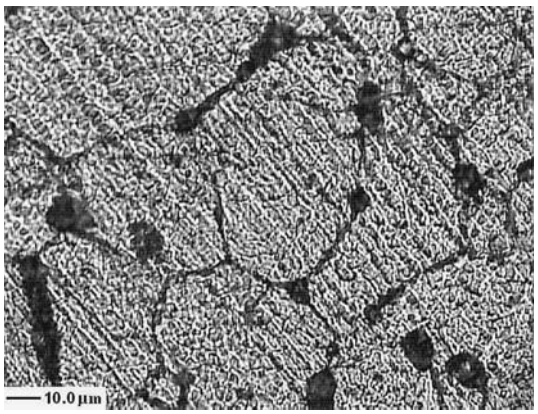

Fig. 4 Microstructure of the solution treated sample after the EPR-DL test showing intergranular attack

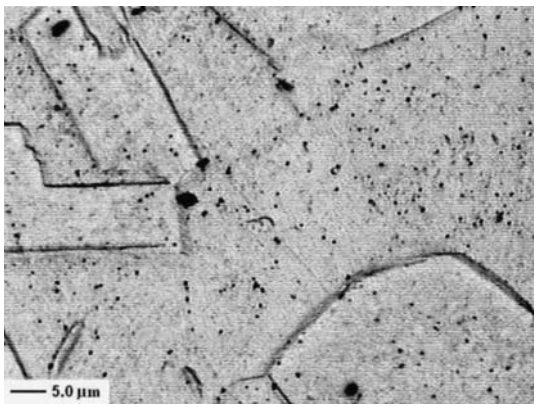

Fig. 5 Microstructure of the sample stabilized at 875 °C and aged at 600 °C for 100 h. Electrolytic etch in oxalic acid solution

respectively. Coarse intergranular TiC particles are clearly observed. Chromium carbide precipitation was not observed at these conditions and the I_r/I_a ratio resulted below 0.005 (see EPR-DL curve in Fig. 7).

Figure 8 shows the hardness variation with stabilization treatment. The fine TiC precipitation at 850 °C increases the hardness from 154 HV in the solution treated condition to about 165 HV, which is relatively maintained in the stabilization treatments at 875 °C and 900 °C. The increase of the stabilization temperature from 900 °C to 975 °C causes softening due to the coarsening of the TiC precipitates as seen in Fig. 6(a) and (b). A minimum hardness value is obtained in the sample treated at 975 °C. A small hardening is then observed with treatments at 1000 °C and 1025 °C due to partial dissolution of TiC carbides and the solid solution strengthening of carbon.

The use of as high as possible stabilization temperatures is one of the solutions found to avoid the re-heating cracking in Ti and Nb stabilized steels [5]. A careful investigation of samples stabilized at 975 °C and 1000 °C

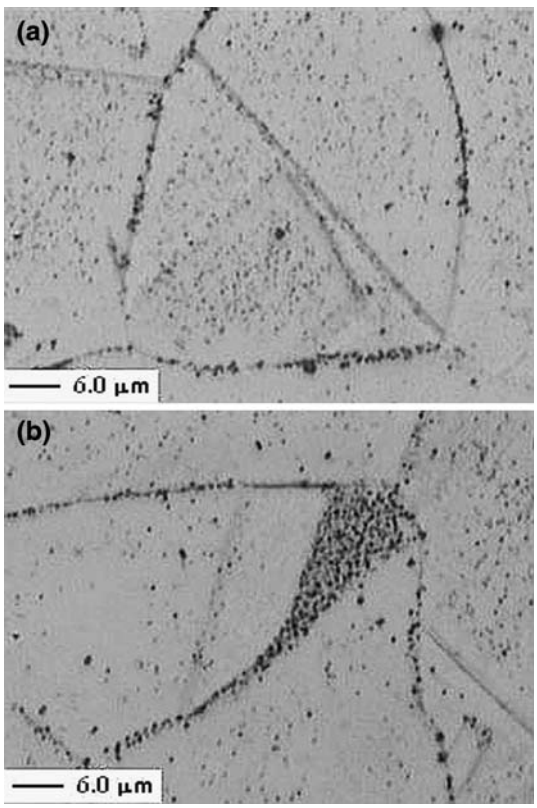

Fig. 6 Microstructure of the sample stabilized at 950 °C and aged at 600 °C for 24 h (**a**) and 100 h (**b**). Electrolytic etch in oxalic acid solution

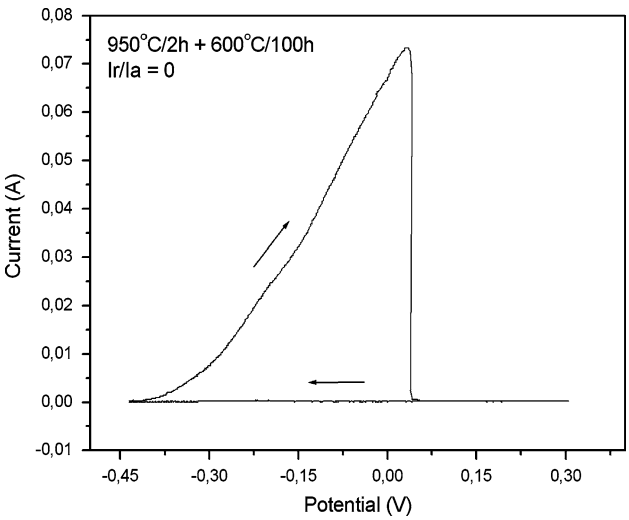

Fig. 7 EPR-DL curve of the sample at 950 °C and aged at 600 °C for 100 h

was so carried out to find the maximum permissible stabilization temperature for the AISI 321 steel.

The sample stabilized at 1000 °C and aged at 600 °C for 24 h did not present any sign of sensitization. However, increasing the aging time at 600 °C to 100 h, the very

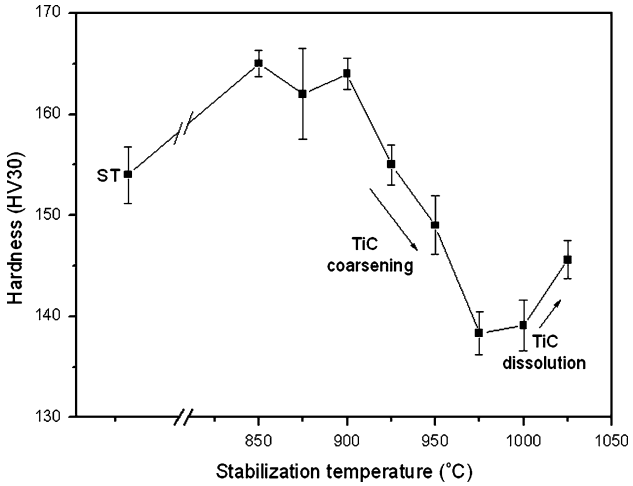

Fig. 8 Hardness against stabilization temperature

beginning of the sensitization process can be observed by microscopy (Fig. 9). The small holes in the grain boundaries are from $Cr_{23}C_6$ particles, which were removed by the electrolytic etch in oxalic acid solution (ASTM 262-practice A). The EPR-DL curve at this condition also shows a small reactivation peak (Fig. 10) and a I_r/I_a ratio equal 0.02.

The behavior of the samples stabilized at 975 °C is similar to those treated at 1000 °C. Chromium carbides are not observed in the sample aged at 600 °C for 24 h, but some intergranular holes, typical of $Cr_{23}C_6$, can be seen in the one aged for 100 h, as shown in Fig. 11. The I_r/I_a ratio at this condition was 0.01. According to some authors [4, 6], the I_r/I_a can be related to three microstructures cited in the ASTM A262 standard [2] as follows: $I_r/I_a < 0.001$—step; $0.001 < I_r/I_a < 0.05$—dual; $I_r/I_a > 0.05$—ditch (completely sensitized).

Figure 12 shows the I_r/I_a ratio against stabilization temperature for samples aged at 600 °C for 24 h and 100 h.

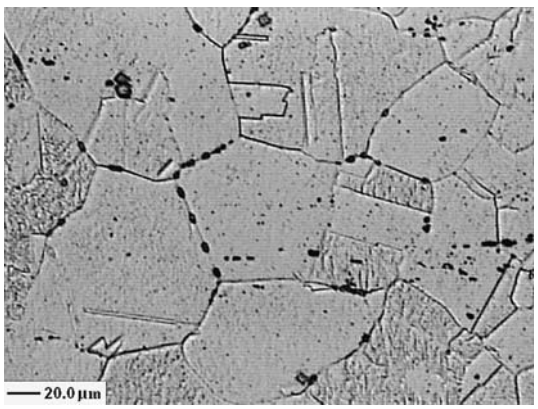

Fig. 9 Sample stabilized at 1000 °C and aged at 600 °C for 100 h. Electrolytic etch in oxalic acid solution

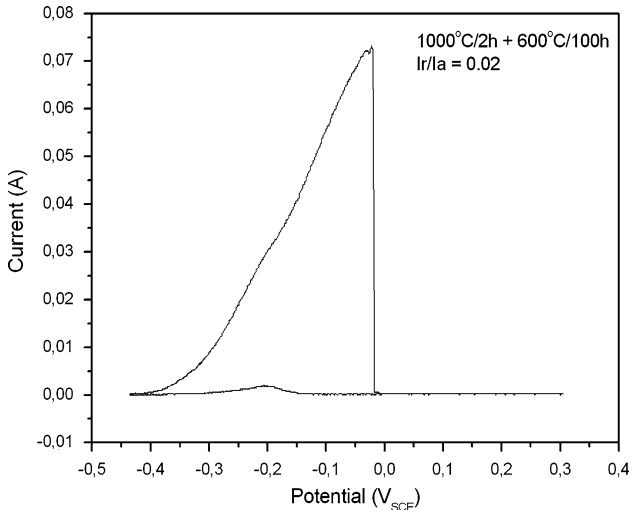

Fig. 10 Solution treated at 1,000 °C and aged at 600 °C for 100 h

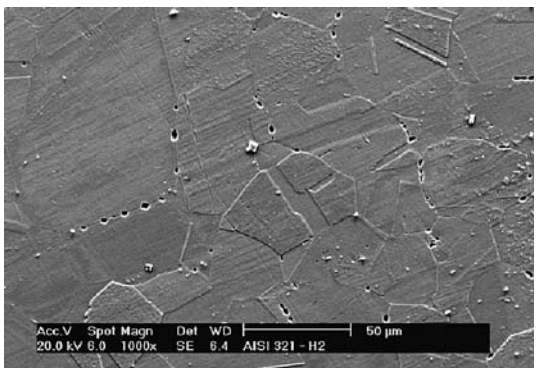

Fig. 11 Sample stabilized at 975 °C and aged at 600 °C for 100 h. Electrolytic etch in oxalic acid solution

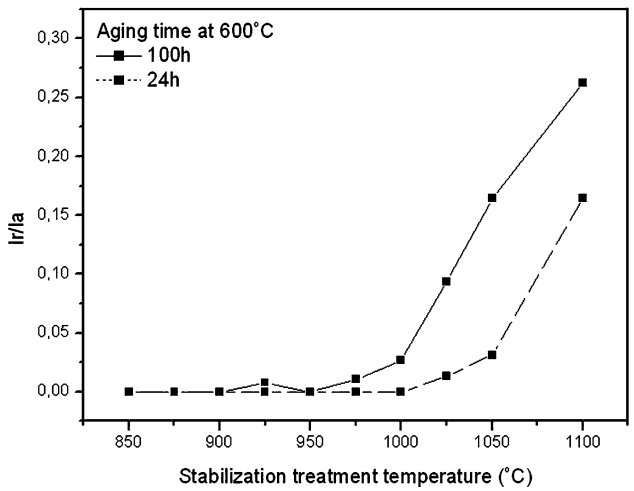

Fig. 12 I_r/I_a ratio against stabilization temperature for samples aged at 24 h and 100 h

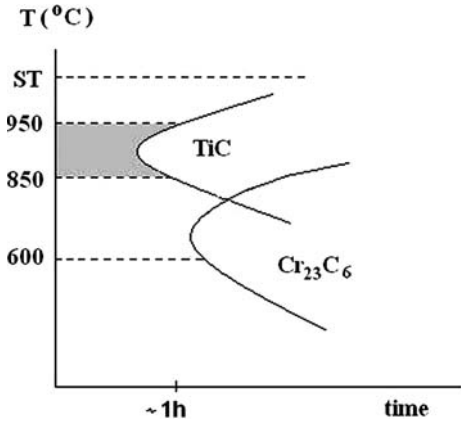

Fig. 13 TTT schematic curves for TiC and $Cr_{23}C_6$ precipitation

In a previous work, Sousa et al. [7] found that the stabilization was effective at 900 °C but not at 1000 °C. The results presented in this work show that the stabilization treatment can be carried out at temperatures as high as 950 °C. The results of the samples stabilized at 975 °C or 1000 °C, and aged at 600 °C for 100 h, show the very begin of the sensitization process at these conditions.

From the thermodynamic data provided by Padilha and Guedes [8] the equilibrium of the 23/6[Cr] + [C] $\rightarrow$ 1/6<$Cr_{23}C_6$> reaction for an austenitic stainless steel with 17%Cr gives a %C = 0.0004% into solid solution at 600 °C and 0.0265% at 900 °C, which shows that the chromium carbide precipitation is extremely favorable at 600 °C but not at 900 °C. From the equilibrium of the [T] + [C] $\rightarrow$ <TiC> reaction the solubility product can be calculated by Eqs. (1) and (2):

$$\ln [Ti].[C] = 8.86 - \frac{24236}{T} \quad (T \geq 1155\,\mathrm{K}) \tag{1}$$

$$\ln [Ti].[C] = 8.48 - \frac{23808}{T} \quad (298 > T < 1155\,\mathrm{K}) \tag{2}$$

The solubility product [Ti]·[C] is the amount of Ti (wt%.) multiplied by the amount C (wt%.) into solid solution at the equilibrium. Using Eqs. (1) and (2), this product decreases from 0.00015 at 1100 °C to 1.75×10^{-5} at 950 °C and 6.9×10^{-9} at 600 °C which shows that the TiC formation is also more favorable at 600 °C. However, temperature-time-transformation (TTT) curves from the literature [9] show that the kinetics of $Cr_{23}C_6$ precipitation is faster at 600 °C than the MC carbides. This is the main reason to do the stabilization treatment in the 850–950 °C range before the use into the 600–800 °C interval. The increase of the stabilization temperature above a certain limit (~950 °C) leaves high titanium and carbon contents into solid solution, which enables the $Cr_{23}C_6$ in services at ~600 °C.

A schematic temperature-time-transformation curve (TTT diagram) is shown in Fig. 13. The exact time position of the curves depends on the chemical composition of the steel. The $M_{23}C_6$ precipitation is retarded by the reduction of the carbon content into solid solution while the kinetics and thermodynamic of TiC formation are favored by an excess of Ti in the steel (at%. Ti $\approx$ 1.2 at%.C).

Conclusions

The intergranular corrosion resistance of the AISI 321 steel was evaluated by DL-EPR tests and metallographic examination. In the solution treated condition (1100 °C, water quenched) a high degree of sensitization (I_r/I_a) was measured (I_r/I_a = 0.17) and intergranular chromium carbide precipitation was detected. The stabilization treatment in the 850 °C to 950 °C was effective to prevent sensitization at 600 °C till 100 h of exposition. Coarse precipitates produced by the stabilization at 950 °C prevents the chromium carbide precipitation and do not harden the material. The samples stabilized at 975 °C and 1000 °C, and aged at 600 °C for 100 h, showed the very begin of the sensitization process.

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