Investigation on Intergranular Corrosion Behaviour and optimization of Stabilization Heat Treatment Temperature of 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℃), 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 determined by means of microscopy and double loop electrochemical potentiokinetic reactivation (DL-EPR) test. Thus after solution annealing at 1080℃ for 90 min, the samples stabilized at temperatures in 800–1025℃ range and then sensitized at 675℃ up to 110 hr. It was found that the higher temperature for stabilization must be 900℃. Samples stabilized at higher than 900℃ had higher susceptibility to intergranular corrosion. From obtained hardness profile, critical stabilization temperature that there is no risk of sensitization was also determined.

Keywords: AISI 321stainless steel, Sensitization, Intergranular corrosion, Electrochemical DL-EPR test.

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 presence of intergranular TiC and NbC fine precipitation in austenite matrix has double functions: they prevent sensitization and intergranular corrosion and also improve the creep resistance of the steel.

Therefore, the austenitic steels must be heat treated at high temperatures before use at 600–800℃ [1]. 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

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chromium in solid solution during the high temperature service. The ASTM A358/358M standard [2] states that the customer and the manufacturer must mutually agree on the temperature for stabilization treatment.

The focus of the present work was to evaluate the importance of the stabilization heat treatment on the intergranular corrosion resistance of the AISI 321 steel subjected to long periods of aging at 675℃. Seven stabilization temperatures in the 800℃ to 1025℃ range were tested in order to find the best temperature range. Before electrochemical tests, samples were sensitized for a long period up to 110 hr. Microscopy and double loop electrochemical potentiokinetic reactivation (DL–EPR) test were used to find the best stabilization temperature. The degree of sensitization was evaluated by I_r/I_a ratio, where I_a is the peak current density of the anodic scan and I_r is the peak current density of the reversed scan in DL–EPR test [3].

According to some authors [3, 6], the I_r/I_a can be related to three microstructures cited in the ASTM A262 standard [4] as follows: $I_r/I_a < 0.001$—step (low sensitized); $0.001 < I_r/I_a < 0.05$—dual (medium sensitized); $I_r/I_a > 0.05$—ditch (completely sensitized). The effect of the stabilization treatment on the hardness was also determined.

Experimental

The AISI 321stainless steel studied in this work was the forged bar with 300 mm diameter. The Solution annealing treatment at 1080℃ for 90 min performed and followed with water quenching. The chemical composition is shown in Table 1. Samples were cut from the solution treated bar with 25×25×2.5 mm dimensions and and stabilized in air at 800℃, 825℃, 850℃, 875℃, 900℃, 950℃ and 1025℃, for 2 hr, followed by air cooling. After stabilization treatments the samples were sensitized at 675℃ for selected times up to 110 hr. The samples were electrolytically etched in oxalic acid solution, as described in the ASTM A262 standard (practice A) [4] and the microstructures were observed in optical and scanning electron microscopes.

Table1. Chemical composition of the AISI 321 stainless steel (wt%)

C	Cr	Ni	Ti	Si	Mn	N
0.065	17.42	8.54	0.573	0.68	1.92	0.0178

The intergranular corrosion resistance was investigated by double loop electrochemical potentiokinetic tests (DL– EPR) [3]. These tests were conducted in a conventional three electrode cell using graphite as the auxiliary electrode and a saturated silver–silver chloride

electrode (Ag/AgCl) as the reference one. Prior to each experiment, the working electrodes were polished with grid 400, 600, 800 and 1000 emery paper respectively, degreased with alcohol and cleaned in water. The electrolyte was 0.5 M H_2SO_4 + 0.01 M KSCN solution. 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_{ocp}) had developed (about 10 min) followed by the potential sweep in the anodic direction at 1.66mV s^{-1} until the potential of 0.35 $V_{Ag/AgCl}$ was reached, then the scan was reversed in the cathodic direction until the E_{ocp}. The degree of sensitization was evaluated by the ratio I_r/I_a, where I_a is the peak current density of the anodic scan and I_r is the peak current density in the reversed scan.

In order to find relation between hardness and dissolution and growth of TiC particles in austenite matrix, Vickers hardness tests with 30 kgf load (HV30) in all stabilized samples were also carried out.

Results and discussion

Figure 1 shows the microstructure of the sample in the solution treated condition. This is a ''step'' microstructure indicates loss in intergranular $Cr_{23}C_6$ Carbides precipitation and intergranular attack [4], containing coarse and square shaped TiN particles (indicated by arrows). The solution treatment was dissolved the all of chromium carbides that maintained in matrix from production processes.
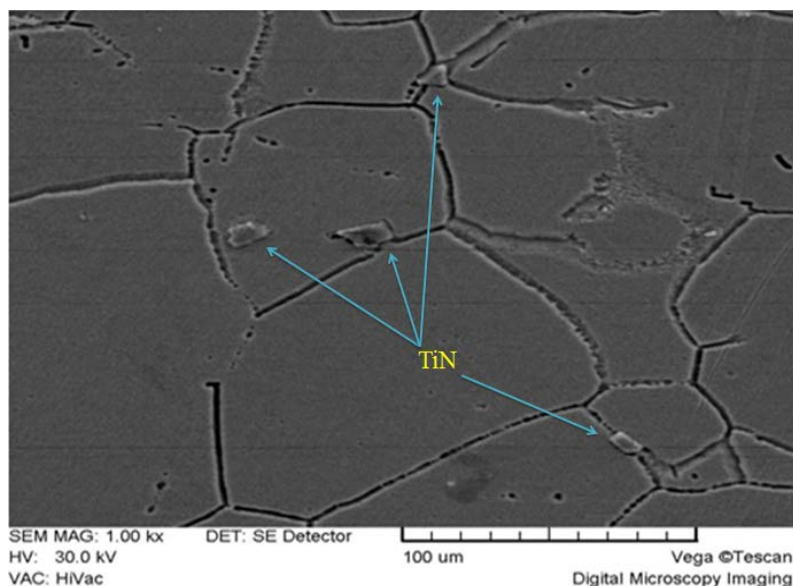

Fig. 1 Solution treated sample. TiN particles are indicated by arrows

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Figure 2 shows the sample which was sensitized at 675℃ for 35 hr without previous stabilization. The intergranular carbides precipitation is revealed by the electrolytic etch. The DL-EPR curve at this condition (Fig. 3) shows an I_r/I_a=0.49, typical of sensitized material [4]. Figure 4 shows micrograph of this sample just after the DL-EPR test, with the intergranular attack. This examination shows that the AISI 321 stainless steel in the solution treated condition undergoes sensitization at high temperatures in a similar manner as other non stabilized steels. The holes in intergranular of austenite are attributed to chromium carbides. The sample in this condition is non-stabilized and TiC particles are not formed in sufficient amount in matrix because the stabilization treatment had not performed on this sample before sensitization process.
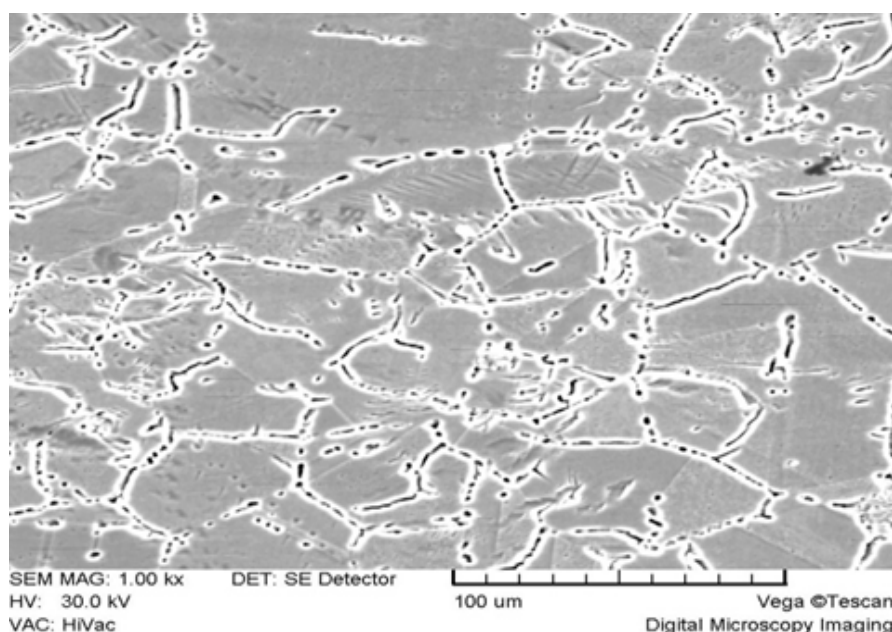

SEM MAG: 1.00 kx   DET: SE Detector
HV: 30.0 kV   100 um   Vega ©Tescan
VAC: HiVac   Digital Microscopy Imaging

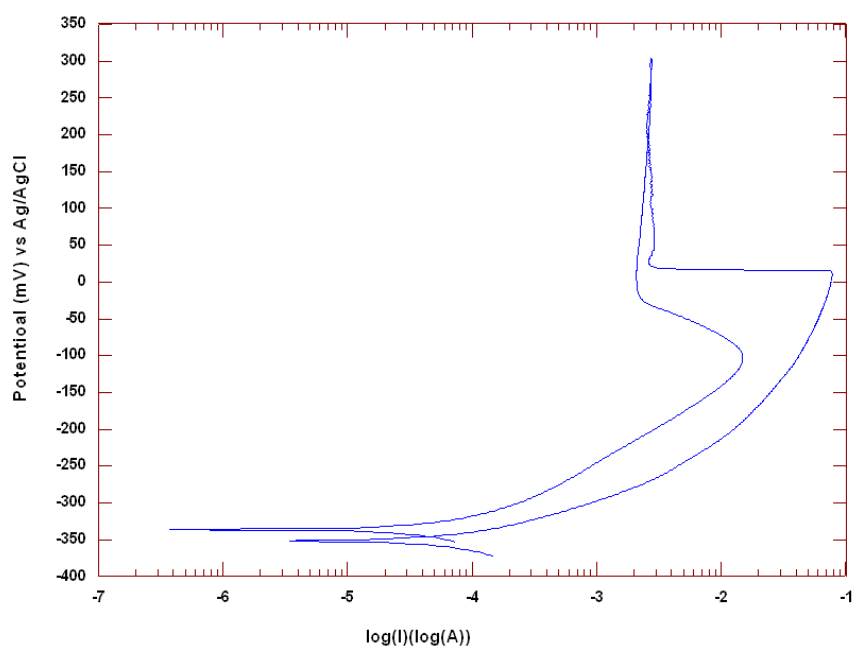Fig. 2 microstructure of sample sensitized at 675℃ for 35 hr without previous stabilization treatment

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Fig. 3 DL-EPR curve of the sample sensitized at 675℃ for 24 hr without previous stabilization treatment
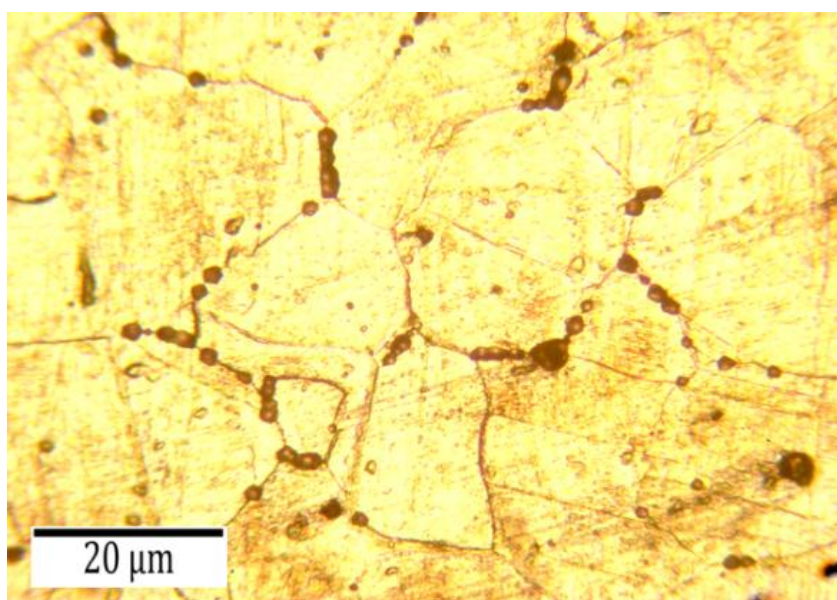

Fig. 4 Microstructure of the solution treated sample after the DL-EPR test showing intergranular attack

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Figure 5 shows the microstructure of the sample sensitized at 675℃ for 110 hr with previous stabilization at 875℃. This shows the dual structure according to ASTM A 262[4] and indicates that stabilization at 875℃ temperature is not completed yet. Figure 6(a) and (b) shows the microstructures of samples stabilized at 900℃ and sensitized at 675℃ for 10 hr and 110 hr respectively. A plenty of coarse intergranular TiC particles are clearly observed. Chromium carbide precipitation was not observed at these conditions and means that after a long time aging at 675℃, the sample has became safe to intergranular carbides precipitation. The resulted I_r/I_a ratio for Fig 6a sample is shown in DL-EPR curve in Fig 7. The degree of sensitization (I_r/I_a) for this sample is 0.03 and comparing with other samples stabilized at different temperatures but similar sensitization condition, is lower one. The sample stabilized at 900℃ and sensitized at 675℃ for 10 hr did not present considerable sign of sensitization. However, increasing the aging time at 675℃ to 110 hr, the increase in sensitization value can be seen by DL-EPR result and microscopy (Fig. 8). The DL-EPR curve at this condition also shows a I_r/I_a ratio equal 0.25 (Fig. 9).
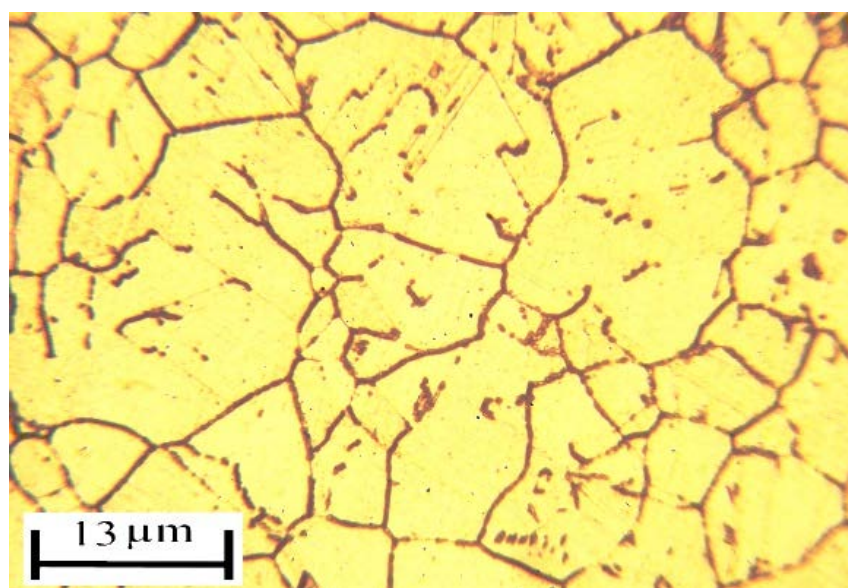

Fig. 5 Microstructure of the sample stabilized at 875℃ and sensitized at 675℃ for 110 hr. Electrolytic etch in oxalic acid solution
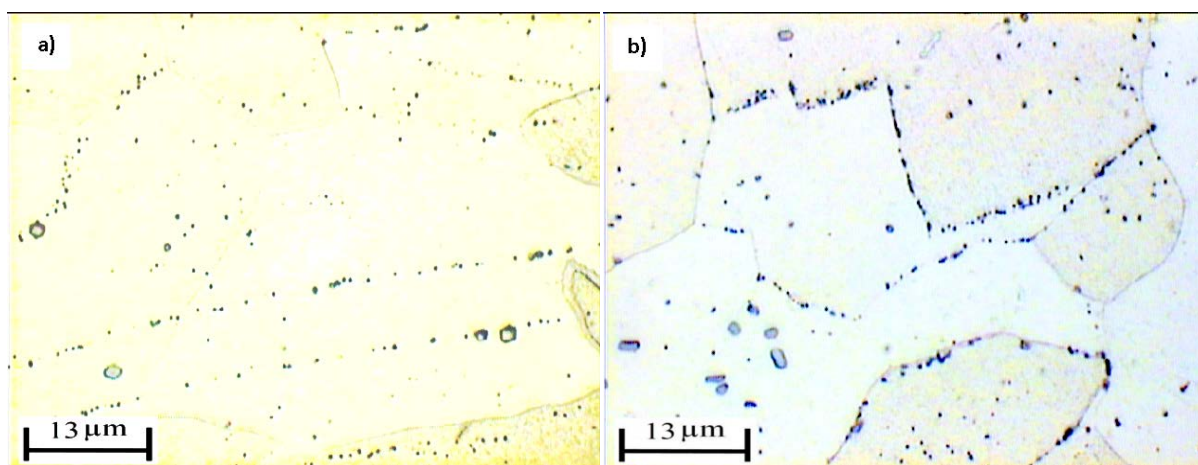
Fig. 6 Microstructure of the sample stabilized at 900℃ and sensitized at 675℃ for 10 hr (a) and 110 hr (b). Electrolytic etch in oxalic acid solution
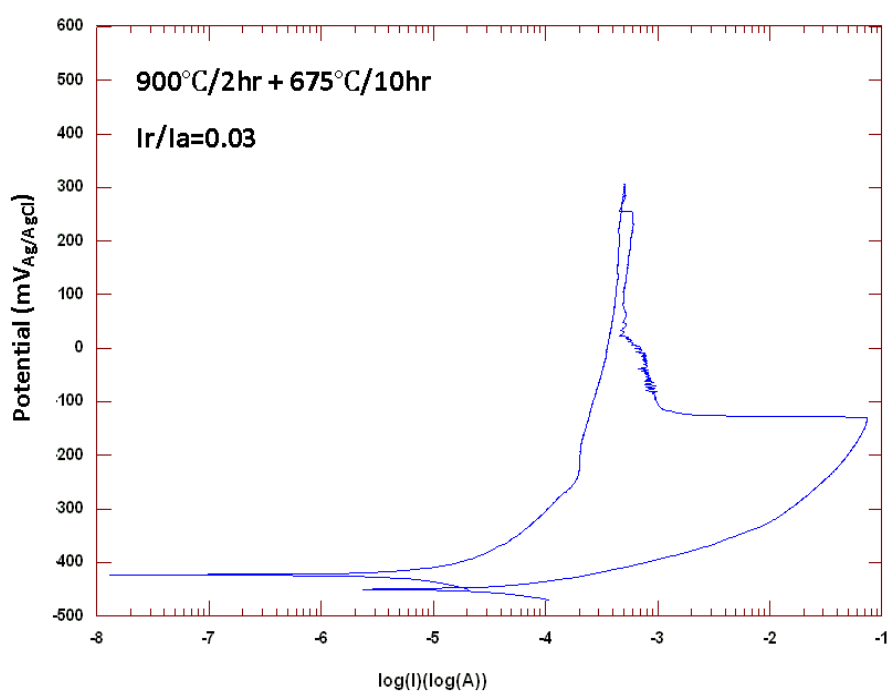

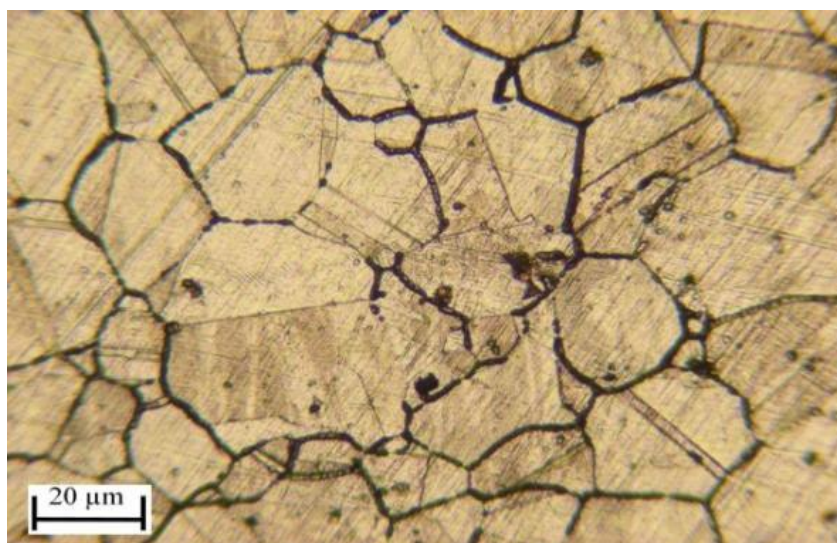Fig. 7 DL-EPR curve of the sample at 900℃ and sensitized at 675℃ for 10 hr

Fig. 8 Sample stabilized at 900℃ and sensitized at 675℃ for 110 hr. Electrolytic etch in oxalic acid solution

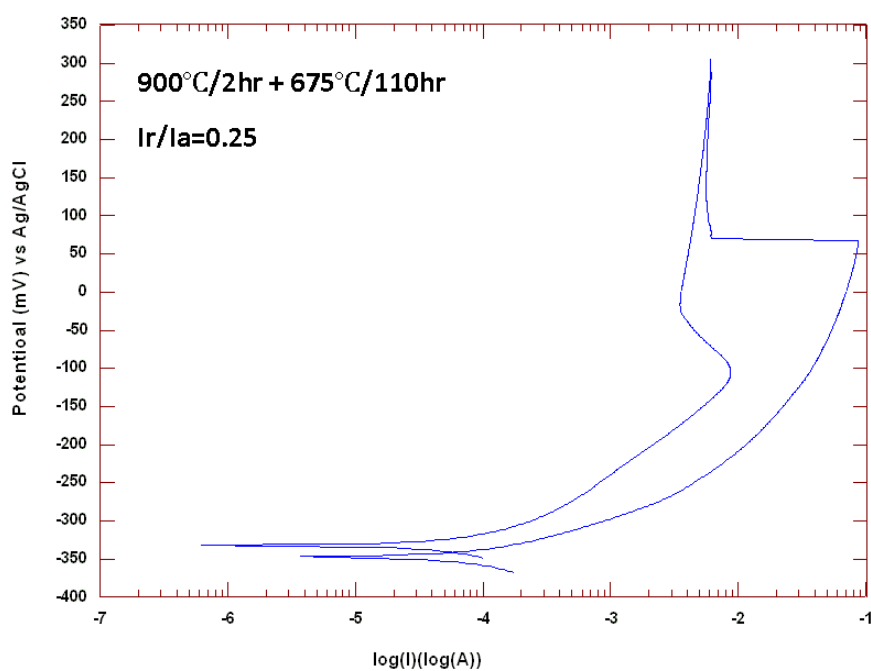

Fig. 9 DL-EPR curve of the sample stabilized at 900℃ and sensitized at 675℃ for 110 hr

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A careful investigation of samples stabilized at 950℃ and 1025℃ was so carried out to find the maximum permissible stabilization temperature for the AISI 321 steel. The small holes in the grain boundaries of these samples are from $Cr_{23}C_6$ particles, which were removed by electrolytic etch in oxalic acid solution (ASTM 262−practice A). The behaviour of the samples stabilized at 950℃ is similar to those treated at 1025℃. Chromium carbides are observed in the sample sensitized at 675℃ for 35 hr, and many intergranular holes, typical of $Cr_{23}C_6$, can be seen in the one sensitized for 110 hr, as shown in Fig. 10. The I_r/I_a ratio at this condition was 0.35. The results of the samples stabilized at 950℃ or 1025℃, and sensitized at 675℃ for 110 hr, showed further sensitization in comparing with sample stabilized at 900℃.

Fig. 10 Sample stabilized at 950℃ and sensitized at 675℃ for 110 hr. Electrolytic etch in oxalic acid solution

The all $I_r/I_a \times 100$ ratios resulted from DL−EPR tests of all the samples are listed in table 2. Figure 11 shows the I_r/I_a ratio against stabilization temperature for samples sensitized at 675℃ for 35 hr and 110 hr. These results can give comparing possibility for select the best condition for stabilization treatment.
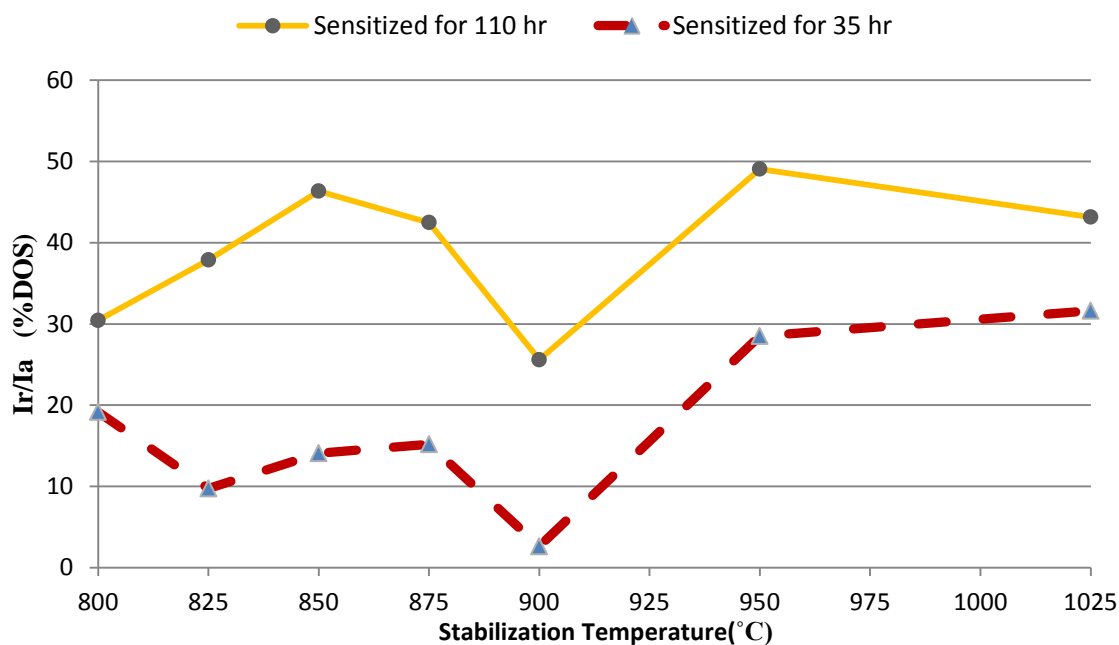
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Fig. 11 %DOS against stabilization temperature for samples aged at 35hr and 100 hr

Table2. $I_r/I_a \times 100$ ratio resulted from DL-EPR tests for all specimens

Specimen	Stabilization Temperature (°C)	Duration of Sensitization Treatment (hr)				
		1	10	35	70	110
1	800	8.71	11.77	19.52	22.01	29.71
2	825	5.23	7.45	9.78	11.98	23.12
3	850	4.47	9.11	14.45	19.78	34.90
4	875	9.22	14.58	15.09	23.69	21.25
5	900	2.56	3.07	3.54	8.58	25.14
6	950	13.88	20.19	24.09	33.78	29.98
7	1025	17.12	18.54	20.46	31.74	43.33
8	–	20.23	33.25	49.22	49.33	49.74

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Thermodynamic analysis

In a previous work, Sousa et al. [7] found that the stabilization was effective at 850℃ but not at higher than this temperature. The results presented in this work show that the stabilization treatment can be carried out at temperatures as high as 900℃. From the thermodynamic data provided by Padilha and Guedes [8] the equilibrium of the 23/6[Cr] + [C] =1/6<Cr23C6> reaction for an austenitic stainless steel with 17%Cr gives a %C = 0.0004% into solid solution at 650℃ and 0.0265% at 900℃, which shows that the chromium carbide precipitation is extremely favourable at 650℃ but not at 900℃. From the equilibrium of the [T] + [C] = <TiC> reaction the solubility product can be calculated by Eqs. (1) and (2):

$$Ln[Ti].[C] = 8/86 - 24236/T \qquad (T \geq 1155K) \qquad\qquad (1)$$

$$Ln[Ti].[C] = 8/48 - 23808/T \qquad (298 > T > 1155K) \qquad\qquad (2)$$

The solubility product [Ti] [C] is the amount of Ti (wt%.) multiplied by the amount of C (wt%.) into solid solution at the equilibrium. Using Eqs. (1) and (2), this product decreases from 0.00015 at 1100℃, to 1.75×10^{-5} at 900℃ and 6.9×10^{-9} at 600℃, which shows that the TiC formation is also more favourable at 600℃. However, temperature-time-transformation (TTT) curves from the literature [9] show that the kinetics of $Cr_{23}C_6$ precipitation is faster at 650℃ than the MC carbides. This is the main reason to do the stabilization treatment in the 850-950℃ range before the use into the 450-800℃ intervals. The increase of the stabilization temperature above a certain limit (~900℃) leaves high titanium and carbon contents into solid solution, which enables the $Cr_{23}C_6$ in services at ~675℃. A schematic temperature-time-transformation curve (TTT diagram) is shown in Fig. 12. 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 favoured by an excess of Ti in the steel.
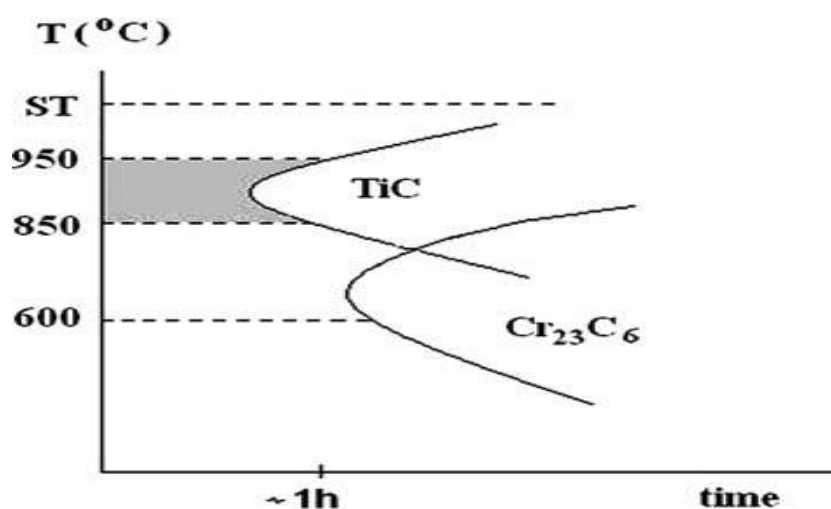
Fig. 12 TTT schematic curves for TiC and $Cr_{23}C_6$ precipitation

Figure 13 shows the hardness variation with stabilization treatment. The fine TiC precipitation at 850℃ increases the hardness from 146 HV in the solution treated condition to about 162 HV, which is relatively maintained in the stabilization treatments at 875℃ and 900℃. The increase of the stabilization temperature from 875℃ to 900℃ 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℃. A small hardening is then observed with treatments at 900℃ and 1000℃ due to partial dissolution of TiC carbides and the solid solution strengthening of carbon. Therefore the stabilization in temperatures higher than 900℃ can be cause TiC dissolution and releases carbon in austenite matrix and eventually leads to chromium carbide forming in austenite boundaries.
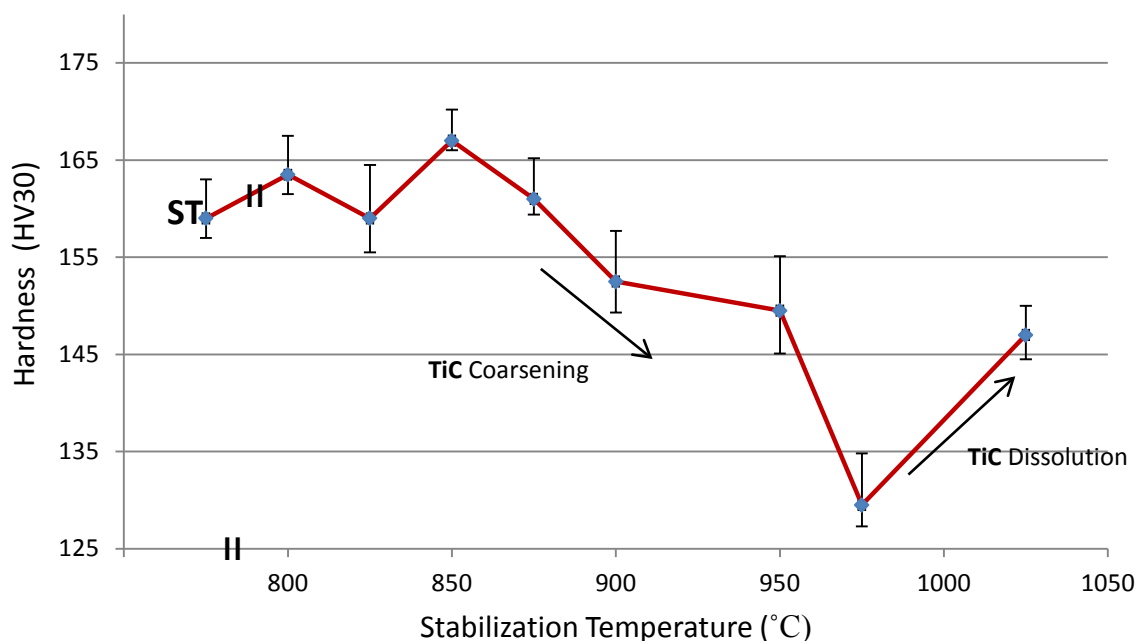
Fig. 13 Hardness against stabilization temperature

Conclusions

- DL–EPR test can be use as a quantative, low expense and fast method for evaluating of intergranular attack in stabilized stainless steels.

- The I_r/I_a ratio of sample stabilized at 900 and aged for 1 hr in 675 was 0.02 and thus is lowest degree of sensitization measured within all cases while in the solution treated condition (1080℃, water quenched) a high degree of sensitization (I_r/I_a) was measured (I_r/I_a=0.49) and intergranular chromium carbide precipitation was detected.

- The stabilization treatment in 900℃ was effective to prevent sensization at 675℃ till 110 hr of exposition. Coarse TiC precipitates produced by the stabilization treatment at 900℃, prevents the chromium carbide precipitation.

- TiC precipitates produced by the stabilization treatment at 900℃, do not harden the material while the samples stabilized at 950℃ and 1025℃, and sensitized at 675℃ for 110 hr, showed the beginning of the sensitization process and comparing hardness in this condition showed that softening occurred. This may be attributed to TiC particle dissolution in austenite matrix.

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