INVESTIGATION ON THE EFFECT OF SOLUTION TREATMENT ON THE INTERGRANULAR CORROSION SUSCEPTIBILITY OF COLD-ROLLED AISI 304 STAINLESS STEEL

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Abstract. *The aim of this work was to study the effect of different solution heat treatments on the intergranular corrosion resistance of AISI 304 stainless steel after cold rolling. Solution treatments were carried out at 1000 ºC, 1050 ºC and 1100 ºC during 1 h. Then, treated specimens were cold rolled producing strips with a thickness reduction of 10% and 40%. After deformation, the specimens were isothermally heated at 675 ºC for 1 hour to induce sensitization. The intergranular corrosion resistance of the sensitized specimens was evaluated by double loop electrochemical potentiokinetic reactivation (DL-EPR) test and by the oxalic acid test based on ASTM A262. The microstructure of the specimens before and after the corrosion tests was observed through SEM micrographs. The results suggest that the best resistance to intergranular attack was for the solution treatment temperature of 1050 ºC.*

Keywords*: AISI 304; intergranular corrosion; solution treatment*

1. INTRODUCTION

AISI 304 stainless steel is widely used in structural applications at chemical and nuclear facilities due to the combination of mechanical and corrosion resistance at a reasonable cost (Aydogdu and Aydinol, 2006; Arutunow and Darowicki, 2008). However, it is well documented that this material is prone to sensitization during welding or thermomechanical processing due to the precipitation of chromium carbides in the intergranular region at temperatures between 450 and 750 ºC. This phenomenon manifests as a result of chromium depletion adjacent to grain boundaries and is known as intergranular corrosion (Kina et al., 2008). Austenitic stainless steels frequently undergo a solution heat treatment before their final use to remove eventual microstructural alterations from previous processing. The degree of sensitization (DOS) may be controlled through such heating treatment procedures (Parvathavarthini et al., 2009; Pardo et al., 2007). This is related to the dissolution of carbides, especially chromium carbides, which may be present and make the material more susceptible to intergranular corrosion and to the control of the nature of the grain boundaries (Jain et al., 2010). Different solution conditions may be used to achieve this goal (Stella et al, 2009; Tavares et al., 2010). A suitable annealing treatment can be used to desensitize austenitic stainless steels and avoid localized corrosion attack (Pal and Raman, 2010). Moreover, it has been reported that plastic deformation strongly affects the degree of sensitization of austenitic stainless steels (Murr et al., 1990). Singh et al. (2008) investigated the effect of different conditions of cold rolling on the intergranular corrosion resistance of AIS 304 stainless steel. They found that DOS increased with deformation. According to the authors, multiplication of crystalline defects such as dislocations after cold work hampered the formation of the chromium-rich passive film on the surface of the stainless steel specimens. Furthermore, chromium carbide precipitation became preponderant at grain boundaries with increasing thickness reduction making the material prone to sensitization. Kain et al. (2004) have also studied the effect of cold work on the sensitization of austenitic stainless steels. They obtained thickness reductions of 15% and 20% by cold rolling. The degree of sensitization increased with plastic straining. This behavior was ascribed to the formation of martensite during cold rolling. Deformation induced martensite has been found to facilitate the precipitation of chromium-rich carbides (Briant, 1982). García et al. (2001) investigated the effects of plastic deformation on the intergranular corrosion resistance of AISI 304 stainless steel. Deformation up to 10% caused severe sensitization of the specimens. According to Trillo and Murr (1999) the decrease of the intergranular corrosion resistance of austenitic stainless steels with increasing plastic deformation is closely related to the nature of the grain boundaries. The susceptibility of stainless steels to intergranular attack may be evaluated by electrochemical techniques such as single loop and double loop electrochemical potentiokinectic reactivation (SL-EPR and DL-EPR). These tests are based on the assumption that only sensitized grain boundaries become active, while grain bodies are unsensitized (Aydogdu and Aydinol, 2006). In the double loop test, specimen is first polarized anodically through the active region. Next, the reactivation scan in the reverse direction is carried out. When it is polarized anodically at a given rate from the corrosion potential to a potential in the passive area, this polarization leads to the formation of a passive layer on the whole surface. When scanning direction is reversed and the potential is decreased at the same rate to the corrosion potential, it leads to the breakdown of the passive film on chromium depleted areas. Two loops are generated from this procedure, an activation loop and a reactivation loop. The ratio of the maximum currents from each loop is the DOS of the material (Lopez et al., 1997). The aim of this work was to study the effect of different solution annealing treatments on the intergranular corrosion resistance of AISI 304 stainless steel after cold rolling through DL-EPR test.

2. MATERIALS AND METHODS

2.1 Material

The nominal chemical composition of the commercial AISI 304 stainless steel plate used in this investigation is reported in Table 1. The dimensions of the specimens were 125 mm x 100 mm x 4 mm.

Table 1. Nominal chemical composition (wt%) of the AISI 304 stainless steel used in this investigation.

C (max)	Si (max)	S (max)	P (max)	Mn	Cr	Ni	Fe
0.08	0.75	0.03	0.04	01/02/00	18.0-20.0	8.0 – 11.0	Bal.

2.2 Solution annealing

The specimens were solution annealed at 1000 ºC, 1050 ºC and 1100 ºC for 1 h under argon atmosphere followed by water quenching.

2.3 Cold rolling

After solution annealing, the specimens were cold rolled at room temperature through a single stand reversion mill. The percentages of thickness reduction were 10% and 40% obtained by successive steps of plastic deformation through the mill.

2.4 Sensitization treatment

Cold worked specimens were then sensitized by heat treatment at 675 ºC for 1 h under argon atmosphere, according to recommendations of the ASTM A-262 standard.

2.5 Microstructural characterization

After the sensitization treatment the grain size of the specimens was determined using the intercept method described in the ASTM E-112 standard. The microstructure of the AISI 304 stainless steel specimens was observed through scanning electron microscopy (SEM) and optical microscopy.

2.6 Intergranular corrosion experiments

2.6.1 Oxalic acid test (ASTM A-262 Practice A)

The oxalic acid etch test consisted of an electrochemical etching of the sensitized specimens in a 10 wt.% oxalic acid solution at a current of 1 $A.cm^{-2}$ for 1.5 min, according to ASTM A-262 Practice A. The etch structure as classified as step, dual or ditch, depending on the degree of sensitization of the material. This procedure was adopted here to compare the results with those obtained from DL-EPR test.

2.6.2 DL-EPR tests

DL-EPR tests were performed according to the recommendations of Majidi and Streicher (1986). The electrolyte was a solution 0.5 M H_2SO_4 + 0.01 M KSCN at room temperature. The electrochemical cell consisted of a conventional three-electrode cell. A saturated calomel electrode (SCE) was used as reference and a platinum wire as counter-electrode. Testing specimens were used as working electrodes. Before the test, specimens were cathodically cleaned for 120 s at a potential of −900mV. Scanning was initiated at -0.5 V versus open circuit potential (OCP) and reversed from potential of +0.2 V (SCE) at a scan rate of 0.167 $mV.s^{-1}$. The % DOS was evaluated by measuring the ratio of $(i_r/i_a)\times100$, where i_r is the peak reactivation current density and i_a is the peak activation current density. The tests were conducted using a potentiostat/galvanostat Autolab PGSTAT 100.

3. RESULTS AND DISCUSSION

3.1 Oxalic acid test

There are three classifications for the microstructures of sensitized austenitic stainless steels after the oxalic acid test: ditch structure, step structure and dual structure. Ditch structure is typical of materials with low resistance to intergranular corrosion. Ditches are formed between grains due to the precipitation of highly cathodic chromium carbides during the sensitization of the specimen. Step structure is typical of high intergranular corrosion resistance materials. No ditches are observed between grains. Dual structure is an intermediate morphology where some ditches are formed during sensitization but the grains are not completely surrounded by a ditch. This structure is typical of a partially sensitized material.

The intergranular corrosion resistance of the solution annealed AISI 304 stainless steel specimens after 10% and 40% of thickness reduction was assessed through the oxalic acid test. Optical and SEM micrographs of the specimens annealed at 1050ºC for 1h are shown in Fig. 1. The specimens were evaluated based on the presence of ditches after the oxalic acid test as recommended by the ASTM A 262 standard. No signs of intergranular attack were observed in the specimens independently of the the thickness reduction after cold rolling. This result indicates the high resistance to sensitization of the AISI 304 stainless steel specimens. Even at a thickness reduction of 40% no ditches were formed as seen for the specimens annealed at 1050 ºC (Fig. 1b). The main difference between the morphology of the specimens with a cold reduction of 40% and those with a cold reduction of 10% was that the austenite grain size was higher for the more severely deformed specimens. This is clearly seen by comparing Fig. 1b that was obtained from a 40%-reduced specimen with Fig. 1a (10%-reduced specimen). The same findings were observed for the specimens annealed at 1000ºC and 1100ºC. In order to respect the restriction established for the maximum size of the file submitted to the conference we do not present the micrographs of the specimens annealed at 1000ºC and 1100ºC. This visual indication was confirmed by evaluating the ASTM grain size of the specimens using the intercept method described in the ASTM E-112 standard. The results are showed in Tab 2. The previous solution treatment had little effect on the grain size. Plastic deformation, in turn, seems to be the main driving force for the grain growth of the specimens. Nevertheless, the grain growth observed for the 40%-cold-rolled specimens did not influence the microstructure of the sensitized specimens after the oxalic acid test. The step structure was observed for all the specimens.

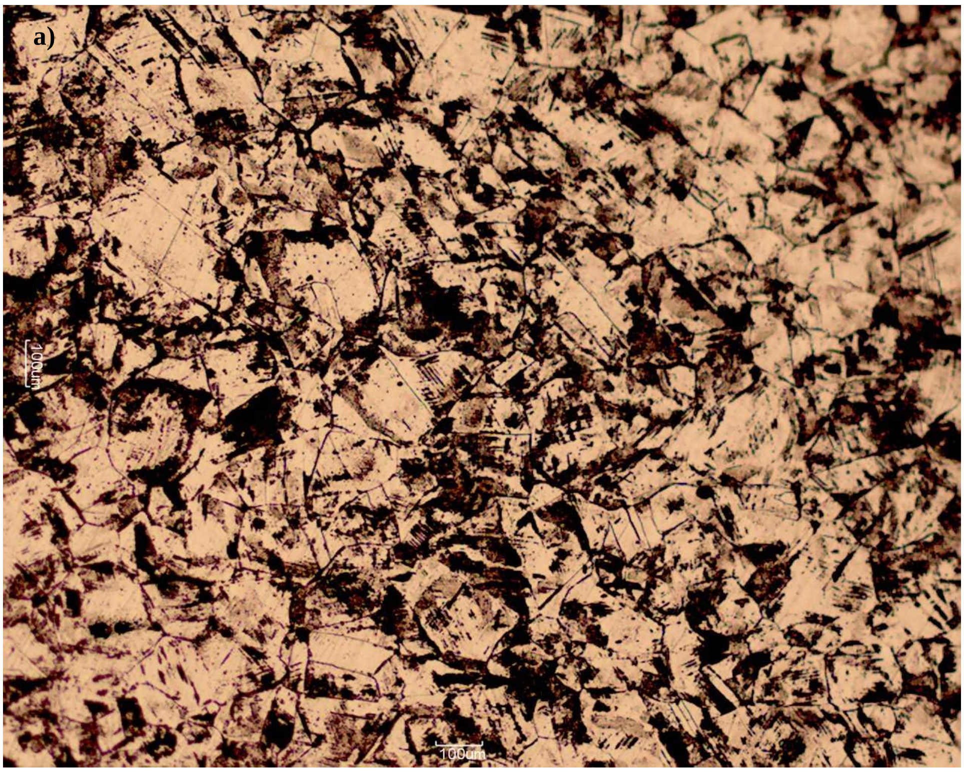
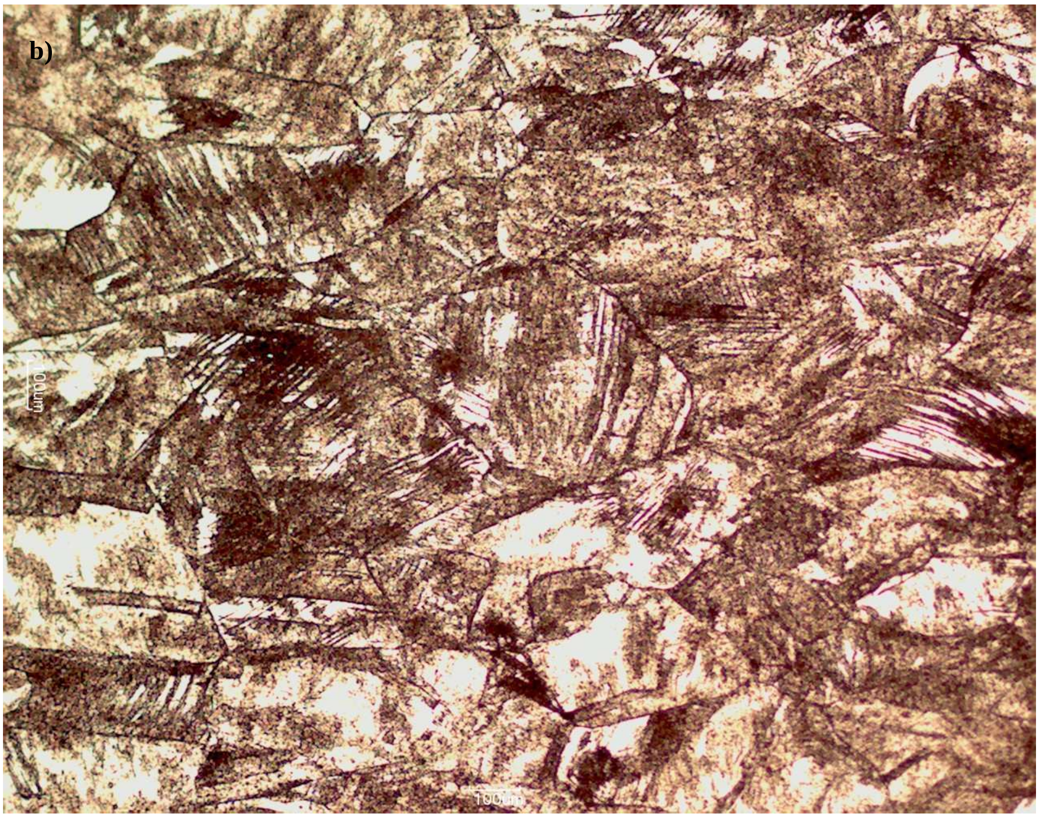


Figure 1. Optical micrographs of AISI 304 stainless specimens: (a) Solution annealed at 1050 ºC for 1h after 10% thickness reduction; (b) Solution annealed at 1050ºC for 1h after 40% thickness reduction. SEM micrographs of AISI 304 stainless steel specimens: (c) Solution-annealed at 1050ºC for 1 h after 10% thickness reduction; (d) Solution-annealed at 1050ºC after a 40% thickness reduction



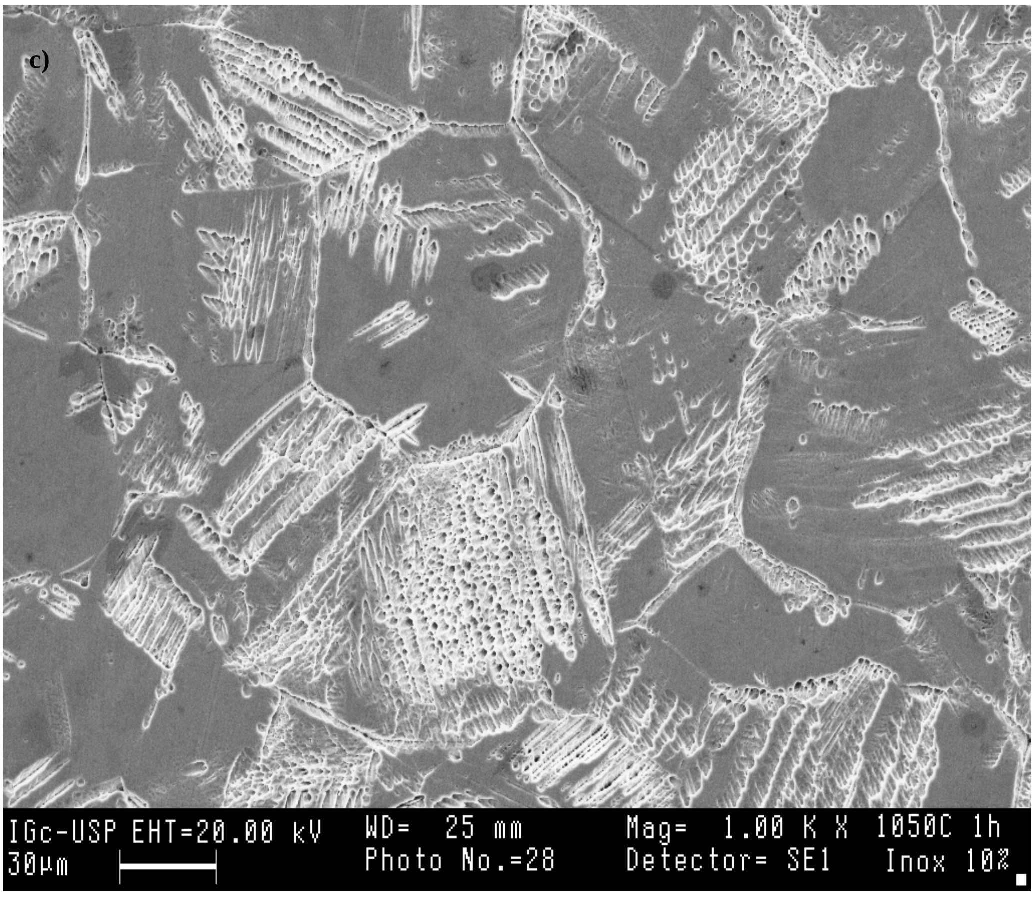


Figure 1. Continued.

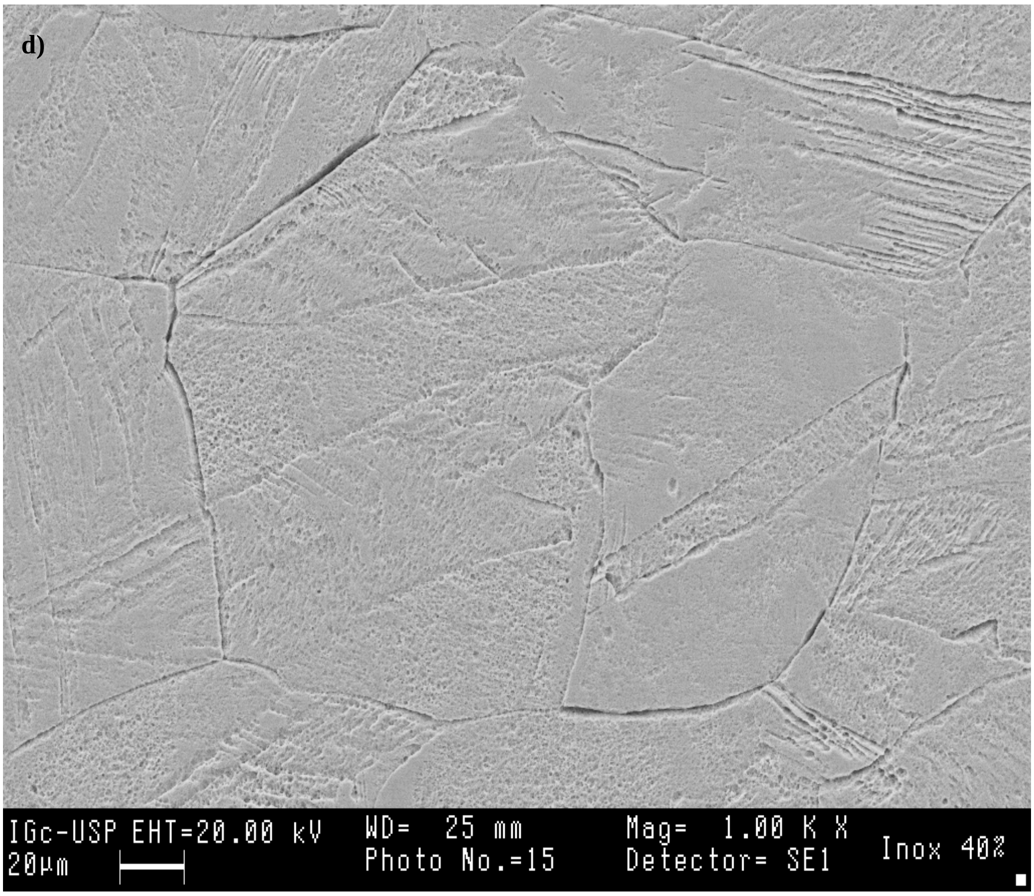


Figure 1. Continued.

Table 2. ASTM grain size (G) of the solutionized AISI 304 specimens after cold rolling (10% and 40% thickness reduction) and sensitization (675ºC for 1 h).

ASTM grain size	Solution treatment					
	1000ºC		1050ºC		1100ºC	
	Reduction		Reduction		Reduction	
	10%	40%	10%	40%	10%	40%
G	3.41	2.17	3.63	2.13	3.74	1.94

Despite the absence of ditches between the twinned austenite grains, it is likely that dislocation density would be higher in the more severely deformed specimens than in the specimens with a cold reduction of 10%. Consequently, the degree of sensitization of the stainless steel specimens would be influenced by the different straining condition of the austenite grains as documented by Murr et al. (1990). However, the oxalic acid test does not point any distinct visual aspect between the specimens. This result may be accepted as an indication of the intergranular corrosion resistance of the AISI 304 specimens. A further investigation by DL-EPR electrochemical technique may give a deeper insight on the influence of solution annealing condition and cold reduction on the degree of sensitization of the AISI 304 stainless steel specimens. This issue is addressed in the next section.

3.2 DL-EPR test

DL-EPR curves obtained for AISI 304 stainless steel specimens after different solution annealing conditions and cold reductions are shown Fig. 2. Values of degree of sensitization (DOS) were calculated from these curves by determining the values of i_a (activation current density peak) and i_r (reactivation current density peak). An example is shown in Fig. 2a. The results are presented in Fig. 3.

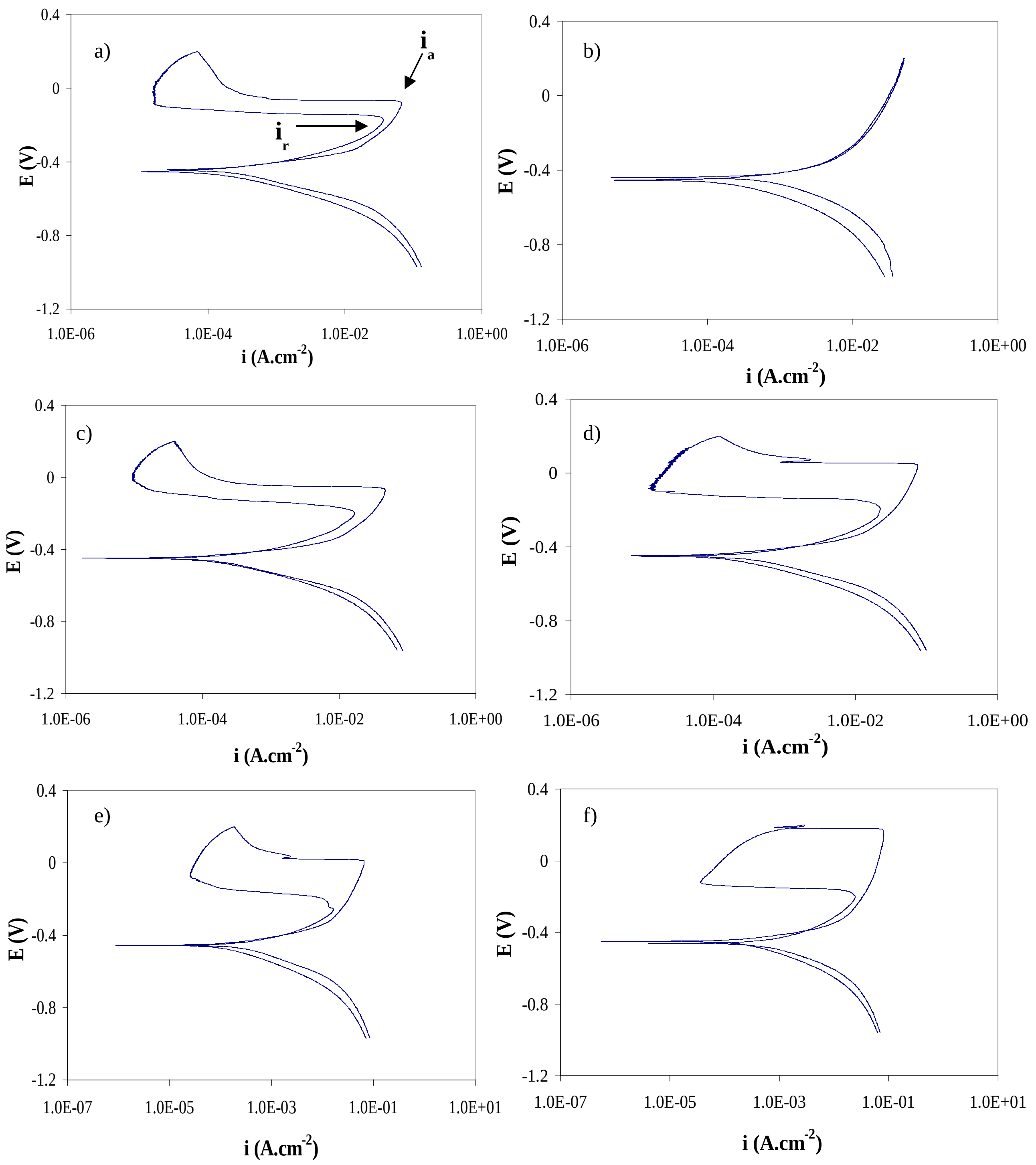


Figure 2. DL-EPR curves of AISI 304 stainless steel specimens: (a) 1000ºC 10%; (b) 1050ºC 10%; (c) 1100ºC 10%; (d) 1000ºC 40%; (e) 1050ºC 40%; (f) 1100ºC 40%.

The specimen solution annealed at 1050ºC with a cold reduction of 10% did not show an increase of anodic current density in the backward curve with respect to the passive current density (Fig. 2b). Therefore, it did not undergo intergranular attack and was not sensitized. When deformation increased to 40% the reactivation peak was present in the DL-EPR curve of the specimen solution annealed at 1050ºC. Thus, as the cold reduction increased so did the degree of sensitization of the material. As discussed by Parvathavarthini et al. (1989) a large increase in dislocation density in the grain boundary region is observed when austenitic stainless steels are subjected to cold work. This will facilitate the precipitation and growth of carbides at grain boundaries when the cold worked material is heated in the critical sensitization range. Cold work leads to the precipitation of finer carbides within smaller inter carbides spacing.

Consequently, the number of carbides at grain boundaries increases with cold work leading to a large number of chromium depleted zones after sensitization. Furthermore, it is possible that stress-induced martensite has formed during cold-rolling of the austenitic matrix. This, in turn, would increase the degree of sensitization of the most severely deformed specimens. Although the formation of martensite was not measured in this work, this effect has been reported in the literature (Kain et al., 2004) and is likely to reduce the resistance of the 304 specimens to intergranular corrosion.

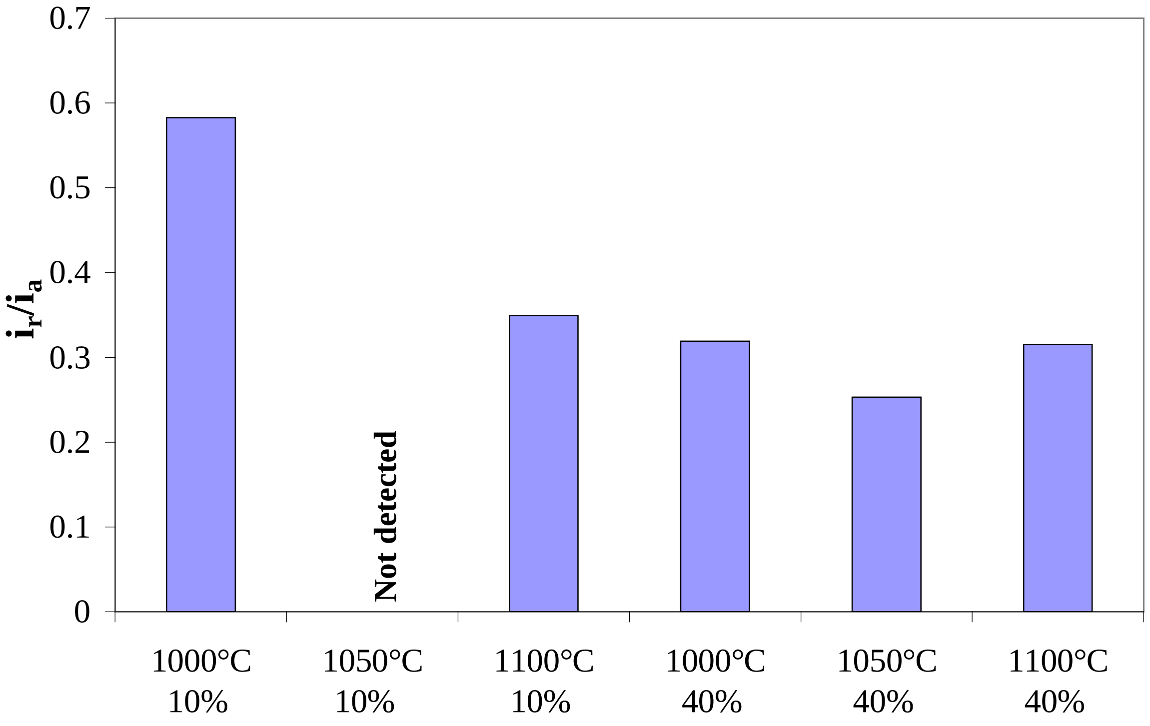


Figure 3. Degree of sensitization (DOS) determined from DL-EPR curves shown in Fig. 2.

Solution annealing at 1000ºC produced materials with the highest DOS, suggesting that at this temperature chromium carbide precipitates were not efficiently dissolved during heat treatment. Solution annealing at 1050ºC produced the best intergranular corrosion resistance. The DL-EPR test exposed the susceptibility of AISI 304 to sensitization allowing for the classification of the different annealing conditions employed in this work while the oxalic acid test did not evidence any significant difference between the morphologies of the different specimens. The reactivation method detects both continuous and local chromium depleted regions while the standard ASTM A262 test exposes only continuous depletion zones. Discrepancies between the results obtained from each test may arise from such different effects that each of them has on the microstructure of the sensitized material.

4. CONCLUSIONS

It's been shown that solution annealing at 1050 ºC is effective at increasing the intergranular corrosion resistance of AISI 304 stainless steel. Deformation may be harmful to sensitization behavior of this material, depending on the solution annealing conducted before cold work. The careful evaluation of DOS after each step of cold work is necessary to guarantee that the material will not become more susceptible to intergranular attack.

5. ACKNOWLEDGEMENTS

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