Influence of the starting condition on the kinetics of sensitization and loss of toughness in an AISI 304 steel

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This work describes the investigation of the embrittlement of AISI 304 steel sensitized at 650°C by Charpy impact test, comparing two starting conditions: (1) mill annealed and machined (MA-M); and (2) solution treated at 1050°C by 1 h followed by oil quenching (ST). The degree of sensitization for both samples was assessed by Optical Microscopy (OM), Scanning Electron Microscopy (SEM) and by Double Loop Electrochemical Potentiodynamic Reactivation test. The results showed that MA-M samples undergo more severe and rapid embrittlement than ST ones and a higher kinetics of sensitization due to small strains concentrated in grain boundaries and α' martensite phase produced during the machining operations. The martensite phase is found to be quite stable at the sensitization treatment at 650°C. The increase of microvoids nucleation at the grain boundaries seems to be the mechanism of embrittlement in the sensitized 304 steel.

1. Introduction

Austenitic stainless steels (ASS), such as AISI 304, are widely used in the petrochemical industry because of their good mechanical properties and corrosion resistance. However, when these materials are submitted to welding process or to operational conditons in the temperature range between 450°C and 850°C, they are very susceptible to intergranular corrosion due to sensitization, which is a process related to the precipitation of the chromium carbide at grain boundaries and chromium depletion in adjacents region [1]. The degree of sensitization (DOS) can be qualitatively evaluated by electrolytic etching with oxalic acid [2] and quantitavely measured by one of the Electrochemical Potentiokinetic Reactivation tests, the Single Loop (SLEPR) or the Double Loop (DLEPR) [1, 3–6].

On the other hand, the embrittlement due to the chromium carbide precipitation at the grain boundaries in ASS has been much less investigated than the loss of corrosion resistance. Hilders and Santana [7] showed that the fracture toughness (K_{IC}) of the AISI 304 SS decreased with the increase of sensitization time at 700°C. The K_{IC} values were obtained by measurements of the dimple size using Scanning Electron Microscopy technique (SEM). Theoretical model was also used to correlate the dimple size with K_{IC}. These authors also found the increase of yeld limit and the decrease of strain fracture with the increase of sensitization time at 700°C. Additionally, it has been shown that the starting condition of the steel plays an important role to the kinetics of carbide precipitation [8–12].

Thus, the present work studies the embrittlement of AISI 304 steel, sensitized at 650°C, by Charpy impact test using microscopy and the DLEPR tests to evaluate the DOS. Two starting conditions were compared: (1) mill annealed in continuous line (using processing conditions of the steelmaker) and machined; and (2) solution treated at 1050°C by 1 h followed by oil quenching.

2. Experimental

2.1. Material and sample preparation

A 3 mm thick sheet of AISI 304 SS was purchased in the hot rolled and mill annealed condition, which the chemical composition is shown in Table I. Charpy-V reduced size samples (2.5 mm thick) were machined according to the ASTM E-23 standard [13]. After machining some samples were solution treated at 1050°C for 1 h in argon atmosphere followed by quench in oil.

TABLE I Chemical composition of the investigated steel in wt%

Element	Cr	Ni	C	N	Mn	S	Fe
wt%	18.05	8.20	0.045	0.0034	1.402	0.001	Balance

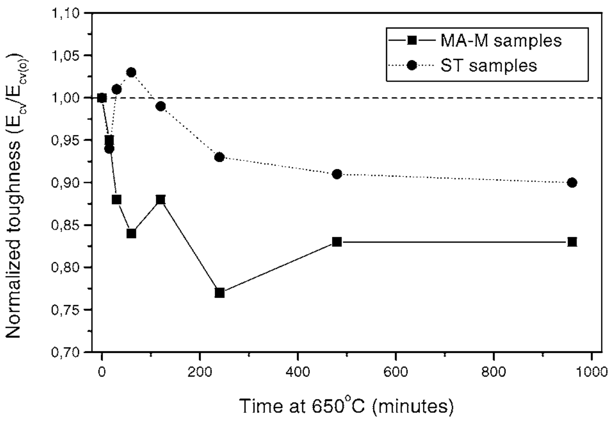

Figure 1 Normalized toughness vs. time of sensitization at 650°C.

Two starting conditions were so investigated: mill annealed and machined (MA-M) and solution treated after machining (ST). MA-M and ST samples were then heat treated at 650°C by different times up to 16 h. After the sensitization treatment the samples were tested at room temperature (25 ± 2°C) in an impact test machine with maximum capacity of 300 J. The error in the energy absorbed values was ±0.5 J. Two samples of each condition were tested and in case of discrepancy higher than 1 J among then, a third sample of the same condition was tested. The values presented are the average ones. Rockwell B hardness tests were also conducted in each condition.

2.2. Physical characterization

Samples for metallography were prepared with electrolytic etching in oxalic acid solution following the recommendations of the ASTM A262 [2]. The surface fractures were observed in a scanning electron microscope JEOL 840A. Samples of the MA-M starting condition were analized before fracture by X-ray diffraction analysis to detect the presence of martensitic phases. This analysis was carried out in a Siemens diffractometer model D5000 using Cu K_{α} radiation.

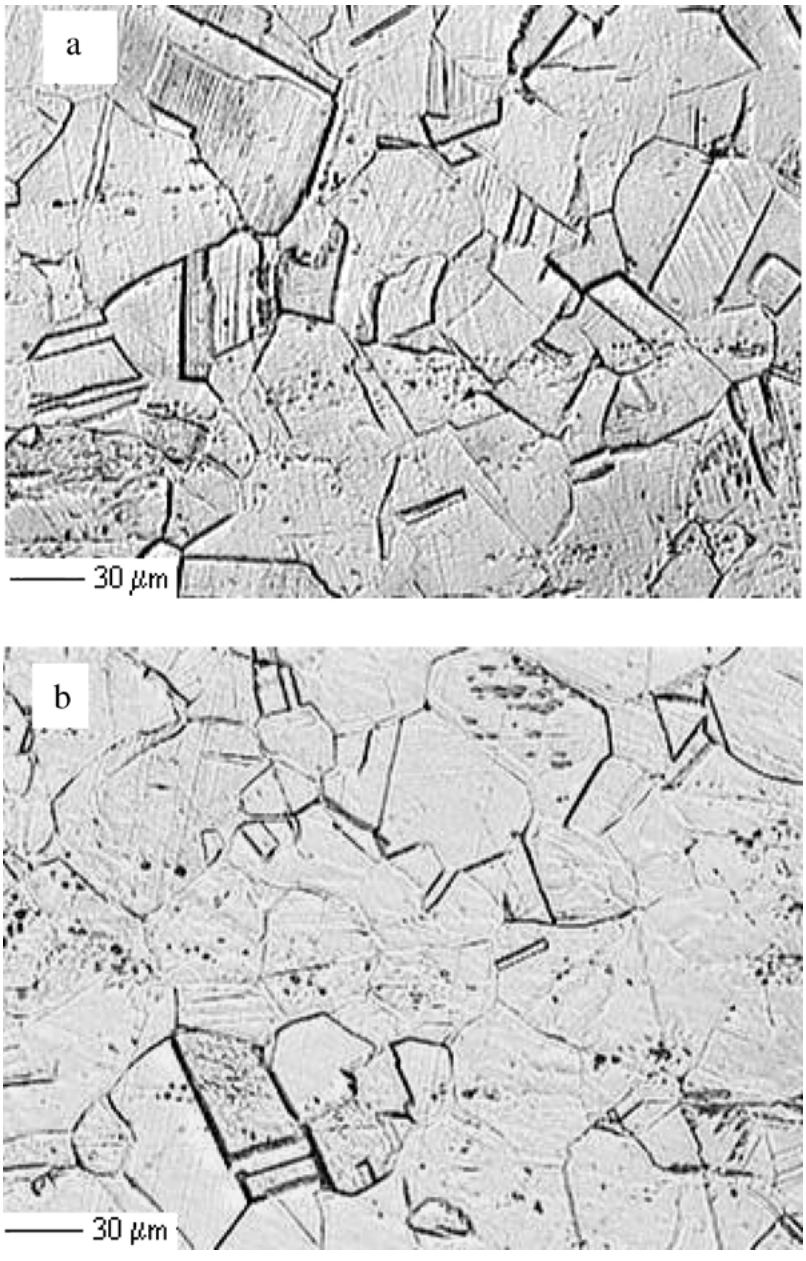

Figure 2 Microstructures of the material: (a) mill annealed and machined (MA-M) and (b) solution treated (ST).

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 AISI 304 samples embedded in epoxy resin. The experiments 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 0.3 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 grid 400 emery paper, degreased with alcohol and cleaned in water. The working solution was 0.05 M $H_2SO_4 + 0.01$ M KSCN (potassium thiocyanate). The DOS 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].

3. Results and discussion

Fig. 1 shows the influence of the time sensitization at 650°C in the normalized toughness (E_{cv}/E_o), which was determined by dividing the adsorbed energy for fracture (E_{cv}) by the adsorbed energy for fracture of the corresponding non-sensitized samples (E_o). The E_o values for MA-M and ST samples were 29 J and 33.5 J, respectively. As can be observed, the embrittlement ratio is decreasing with sensitization time for MA-M samples. For the ST samples, the E_{cv}/E_o initially increases until reaching a maximum at 1 h and decreases for higher time sensitization. These results also show that the MA-M samples undergo a more severe embrittlement process than the ST samples, indicating that the solution treatment improved the mechanical properties of the AISI 304 SS.

Fig. 2 presents the microstructure of the non-sensitized MA-M and ST samples. These micrographs show that both starting condition microstructures do

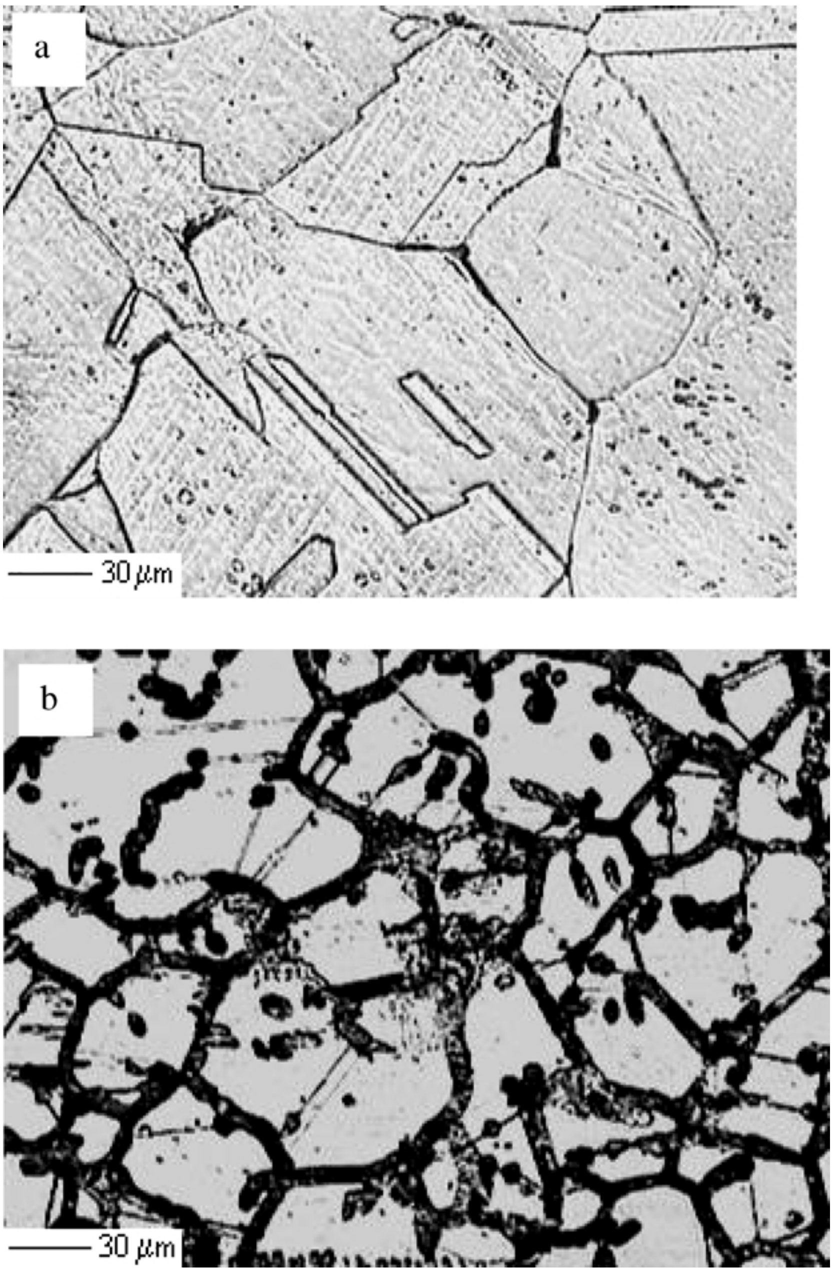

Figure 3 Microstructures of the (a) MA-M and (b) ST samples heat treated at 650°C for 15 min.

not present any carbide precipitation and can be classified as "step" microstructures according to the ASTM A-262 [2]. The measured grain size for the MA-M samples was 35 (±2) μm and those for the solution treated samples was 56 (±2) μm. Despite this, the solution treatment at 1050°C has improved the toughness values.

Fig. 3 shows the microstructures of ST and MA-M samples heat treated at 650°C for 15 min, while the corresponding SEM images are shown in Fig. 4. The analysis of these figures reveal that the MA-M sample shows a microstructure classified as "ditch", while the ST sample presents a "dual" type microstructure with many grain boundaries free of carbide precipitation. Additionally, the ST sample treated for 30 min also presents a "dual" microstructure much less sensitized than the MA-M sample treated for the same time at

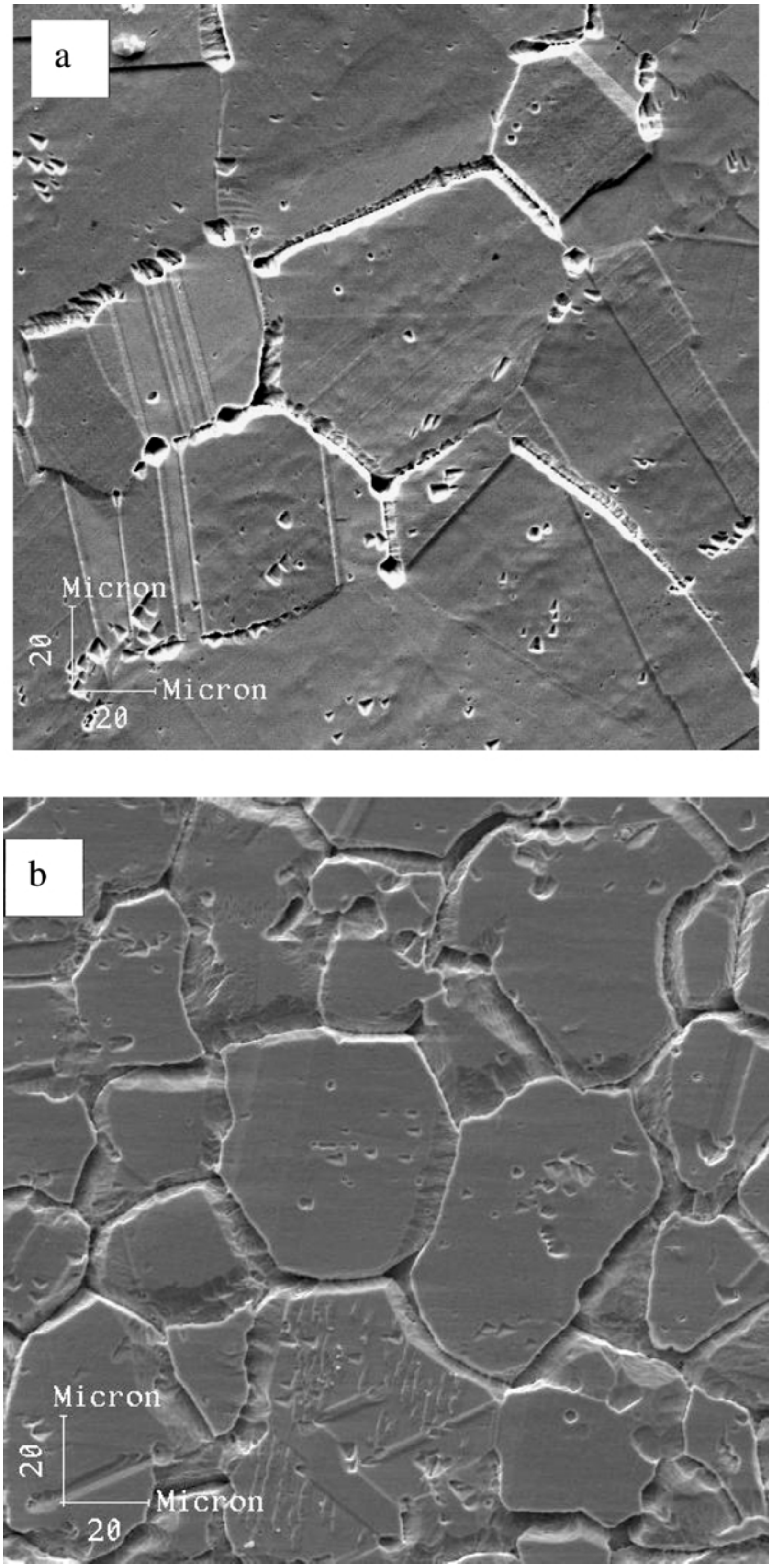

Figure 4 SEM images of the (a) MA-M and (b) ST samples heat treated at 650°C for 15 min.

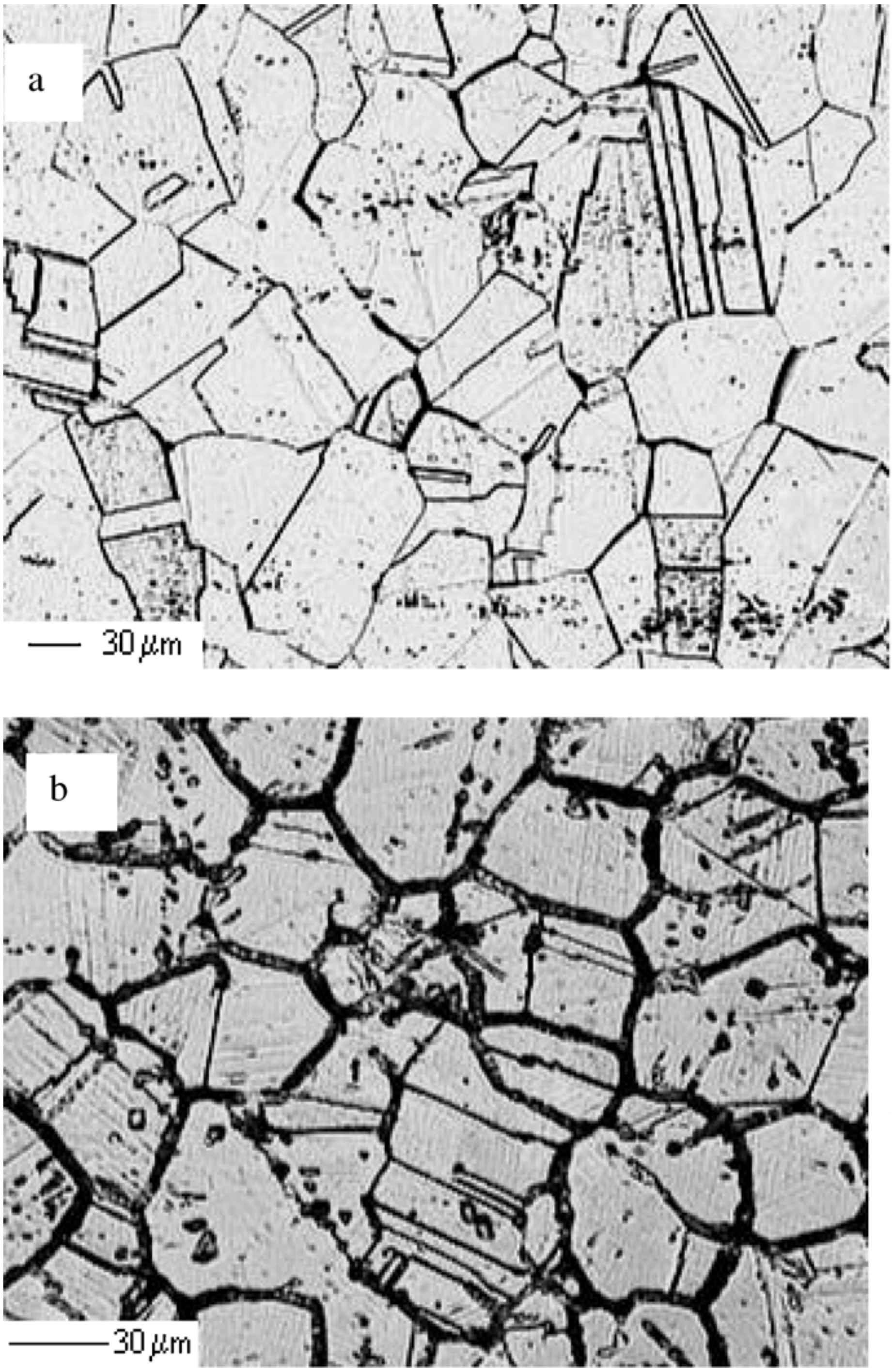

Figure 5 Microstructures of the (a) MA-M and (b) ST samples heat treated at 650°C for 30 min.

650°C, as shown in Fig. 5. It is clearly seen that in the first 30 min the kinetics of precipitation in the MA-M samples is higher than in the ST samples.

The result of DLEPR tests is the ratio between the reactivation current (I_r) and the activation current (I_a). A sensitized material showing a ditch structure should have a current ratio $I_r/I_a > 0.05$ [2]. The I_r/I_a ratio is a measurement of the so called the "degree of sensitization" (DOS).

Fig. 6 shows a typical DLEPR curve obtained for the investigated steel heat treated at 650°C, while in Fig. 7 is shown the influence of the time sensitization in the DOS for both MA-M and ST samples. Fig. 7 shows that the higher DOS value for the MA-M sample is presented for those heat treated for 15 min and 240 min. For the ST sample, the DOS values always increase with time sensitization. According to Majidi and Streicher [14] the values of I_r/I_a ratio in the range of 0.0001 to 0.001 are associated to "step" structure, between 0.001 to 0.05 to "dual" structure and for higher values to "ditch" structure. Thus, these results confirm the higher precipitation kinetics of the MA-M samples.

Murr *et al.* [9] studied the grain boundary structure and observed that the sensitization is strongly influenciated by straining because the effects of strain, especially at lower strains, are likely to be more predominant in grain boundaries. Still accordingly to these authors considerable residual strain is retained in the

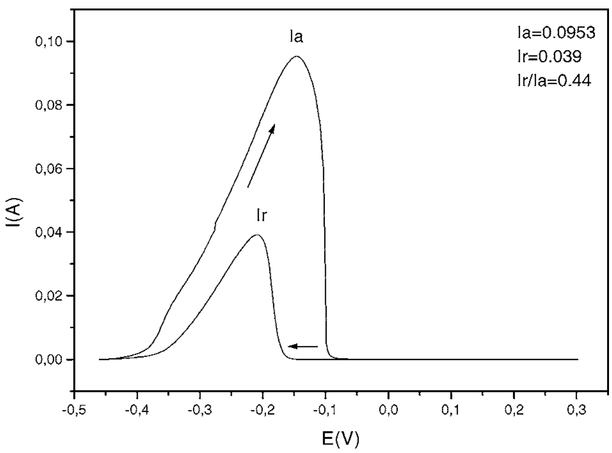

Figure 6 DLEPR curve of the sample MA-M heat treated at 650°C for 15 min.

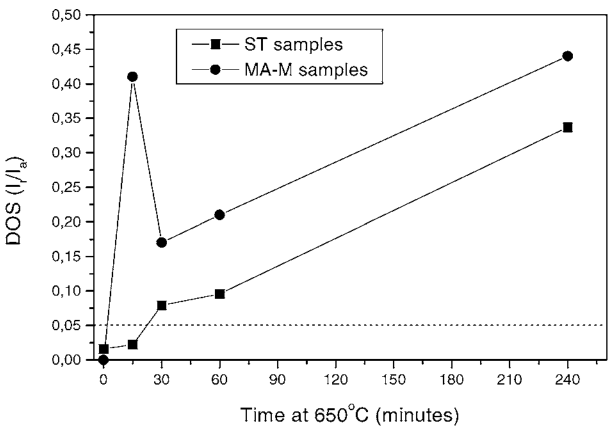

Figure 7 Variation of degree of sensitization (DOS, I_r/I_a) with time of heat treatment at 650°C.

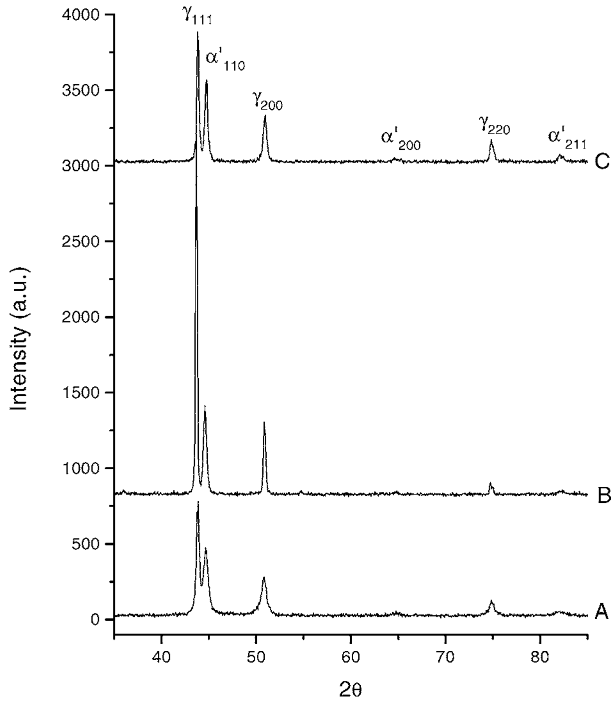

Figure 8 X-ray diffractogram showing α' martensite peaks in the MA-M samples after machining (a), heat treated at 650°C for 15 min and 30 min.

mill annealed samples. Solution treated (ST) samples exhibit a reduced dislocation density and a "cleaner" grain boundary. It was observed that when the strain is small, the dislocation density is much greater near the grain boundaries. The initial straining sensitizes the grain boundary either by activating grain boundaries ledges or creating new ledges. These phenomena increase the chromium diffusivity and enhance carbide nucleation. All these observations made by Murr *et al.* [9] are useful to understand the reason for the different kinetics presented by the two starting conditions, MA-M and ST. The MA-M samples were machined by face milling before aging and this operation has introduced small deformations, which accelerate the kinetics of precipitation.

Fig. 8 shows the X-ray diffraction diagram of the MA-M sample before and after aging by 15 and 30 min. Strain induced α' martensite was generated by the machining operations and was still present after 30 min of ageing at 650°C. This can be also an important feature to consider explaining the differences between ST and MA-M samples. Two factors are important: first, the α' martensite is a bcc structure where the Cr diffusion coeficient is higher than in the fcc austenite phase. Second, the carbide precipitation and sensitization in the AISI 304 SS is accelerated by the creation of a α'/γ fine grained microsctruture by deformation [10, 12]. Trillo *et al.* [11] found that uniaxial deformation in the AISI 304 SS produces intersection martensites which constitute high energy regions and becomes sites for carbide nucleation. When the deformed 304 steel is aged at high temperatures the high energy α' martensite recrystalizes to form intermixed phases of α' and austenite (γ), and $M_{23}C_6$ carbides nucleate and grow in the interphase boundaries created by this recrystalization process.

Comparing Figs 3b and 5b one can say that the MA-M sample heat treated for 15 min is more sensitized than the sample treated for 30 min. The EPR data (Fig. 5) is in agreement with this, since there is a drop in the DOS (I_r/I_a) from 15 to 30 min. The drop of DOS was observed by others authors [11, 12], and is commonly attributed to a desensitization process that occurs due to the chromium diffusion from the rich to the depleted zones. This healing process is favoured by small grain sizes and by straining prior to sensitization [12]. However, Fig. 7 also shows a different behaviour, that is the DOS increase after the drop between 15 and 30 min. Further investigation is needed to explain this.

The effects of α' martensite on the toughness of austenitic stainless steel is not yet well determined, there is a possibility of this phase be responsible for the lower E_{cv} values obtained in the MA-M samples. Although the machining operations induce rather superficial deformations, it must be considered their fundamental importance at the notch-V tip, since this is the crack nucleation region.

The embrittlement effect of the sensitization is related to the increase of microvoids nucleation in the carbides particles [7]. Fig. 9 shows a sequence of interconected small dimples nucleated in the grain boundaries of the steel heat treated at 650°C for 16 h.

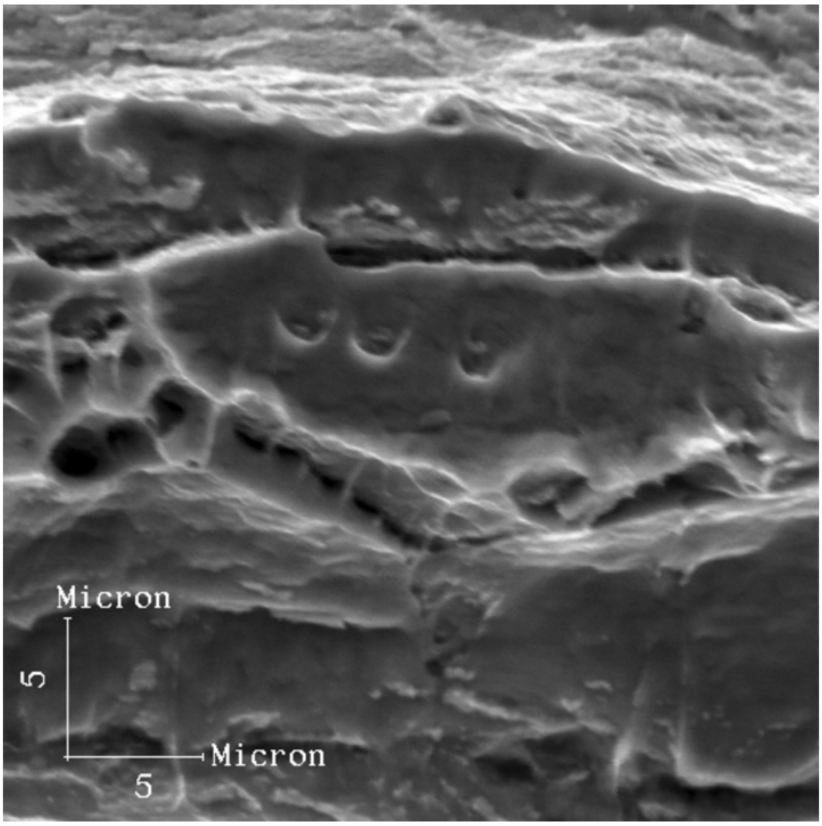

Figure 9 SEM image of the fracture of the MA-M samples heat treated at 650°C for 16 h.

4. Conclusions

The sensitization at 650°C promotes the embrittlement of the AISI 304 steel, as measured by impact Charpy tests. The initial condition, however, plays an important hole in this process. Mill annealed and machined (MA-M) samples undergo more severe and rapid embrittlement than solution treated (ST) ones. MA-M samples also present a higher kinetics of sensitization due to small strains concentrated in grain boundaries and α' martensite phase produced during the machining operations.

The martensite phase is found to be quite stable at the sensitization treatment at 650°C.

The increase of microvoids nucleation at the grain boundaries seems to be the mechanism of embrittlement in the sensitized 304 steel.

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