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Microstructural and electrochemical characterization of the low temperature sensitization of AISI 321stainless steel tube used in petroleum refining plants

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This work describes the behavior of ASTM A312 TP321 tubes heat treated at 600°C for periods of 1, 3, 10, 30, 40, 50, 60, 70, 80, 90, and 100 hours. The degree of sensitization that had occurred was assessed by Scanning Electron Microscopy (SEM) and by the Double Loop Electrochemical Potentiodynamic Reactivation test (DLEPR). The results showed that exposure at 600°C for 80 hours or longer caused severe precipitation of chromium carbides along the grain boundaries characterizing the sensitization of the material despite it being titanium stabilized. In order to minimize the sensitization process, solution annealing in the temperature range of 900–1100°C was studied. Solution annealing at 900°C was the best heat treatment in order to prevent sensitization at 600°C. The solution annealing at 900°C was also effective for samples from tubes that were sensitized after one year of operation in a refining plant. © *2003 Kluwer Academic Publishers*

1. Introduction

Austenitic stainless steels (SS) have been extensively used for desulfurizers in petroleum refining plants because they present good mechanical properties and high corrosion resistance in operational conditions at high temperatures [1, 2]. Among them, AISI 321 SS was developed to avoid the sensitization process, which consists of carbide precipitation at grain boundaries and chromium depletion in adjacent regions, making the material susceptible to intergranular corrosion [1]. This steel contains titanium in order to combine with carbon, therefore avoiding chromium carbide precipitation. However, it was shown by Padilha *et al.* [3] that chromium carbide formation is more favorable than titanium carbide at temperatures around 600°C.

Straus and Huey tests are the most common method to evaluate the susceptibility of the stainless steel to intergranular attack [4]. The first electrochemical method used to evaluate the intensity of sensitization was the Electrochemical Potentiokinetic Reactivation (EPR) method, proposed by Clark [5]. Recently, the use of the Double Loop Electrochemical Potentiodynamic Reactivation (DLEPR) test, proposed by Akashi *et al.* [5], has increased because it is quick, non-destructive, can be used in-situ measurement and it is independent of the surface finishing [1, 5–8].

Thus, this work investigates the increase in intergranular corrosion with the time of heat treatment and the effect of a solution anneal on the intergranular corrosion process in an AISI 321 SS tube using DLEPR test, optical microscopy and scanning electron microscopy.

The background for this study is presented in Fig. 1. It shows the failure of a AISI 321 SS heater tube after slightly more than 1 year of operation. This tube had operated in the temperature range between 350°C and 380°C, but during periods of shutdown for maintenance or failure of operation, the temperature reached 600°C for some hours in different periods of the year. The

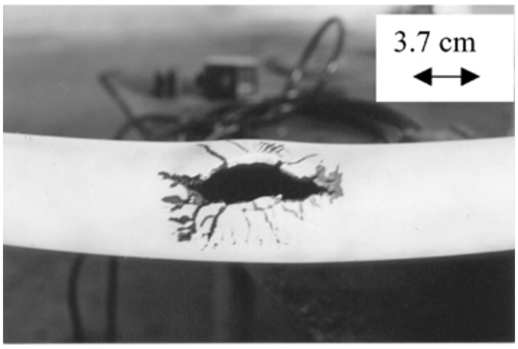

Figure 1 ASTM A312 TP321 heater tube cracked after one year of operation in a petroleum refining industry.

cracks showed a typical case of intergranular stress corrosion cracking (SCS), not occurring near any welded joint.

2. Experimental
2.1. Material and heat treatment
The cracked tube (Fig. 1) and another tube (6.35 cm in diameter) as-received austenitic stainless type ASTM A 312 TP321, with the chemical composition shown in Table I, were used in this investigation. Samples with 1 cm^2 were obtained from both tubes. As-received samples were heat treated in an air furnace atmosphere at 380°C for 100 h and at 600°C for periods of 1, 3, 10, 30, 40, 50, 60, 70, 80, 90, and 100 hours. They were quenched in water and then prepared for metallographic observation and for the DLEPR tests in order to determine the sensitization intensity. In the case of the samples heat treated at 600°C, they were put in a pre-heated furnace, at the same time, at the desired temperature, and after each period of time all of them were quenched in water. One of the samples was then selected for preparation and the others were returned to the furnace and left there until the new period of time was reached. This operation was systematically repeated until 100 hours. The objective of this sequence was to simulate a long period of operation with many shutdowns. Another group of samples from the as-received tube was solution treated at 900°C, 950°C, 1000°C and 1050°C for 75 min and then exposed for 100 hours at 600°C, in order to determine which solution anneal temperature is the best for this material prior to operating at 600°C.

2.2. DLEPR tests
The working electrode was constructed using ASTM A 312 TP321 samples embedded in epoxy resin. The DLEPR tests were carried out at room temperature (≅25°C) in a conventional three-electrode cell using a Pt foil as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference one.

TABLE I Chemical composition of the ASTM A 312 TP321 (wt%)

Element	C	Mn	Si	Cr	Ni	Ti
wt.%	0.05	1.8	0.8	16.7	9.8	0.41

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 0.6 V (vs. SCE) was reached, then the scan was reversed in the cathodic direction until the E_{oc}.

The working solution in this project was 3 M H_2SO_4 + 0,01 M KSCN (potassium thiocyanate) + 1 M NaCl due to preliminary tests showing that the standard solution (0.05 M H_2SO_4 + 0.01 M KSCN) of the DLEPR test was not aggressive enough for the AISI 321 SS. The sensitization intensity 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.

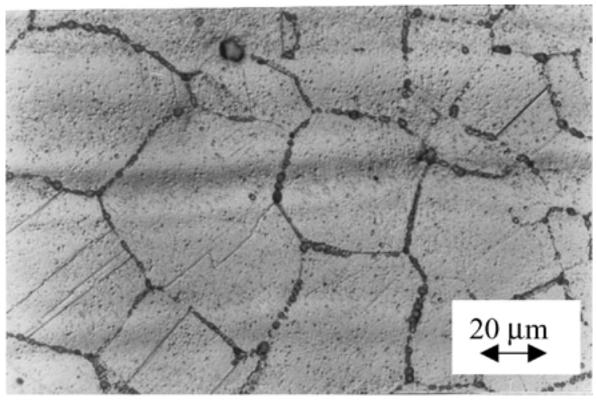

Figure 2 Optical micrograph of a sample from the cracked tube far away from the cracked region.

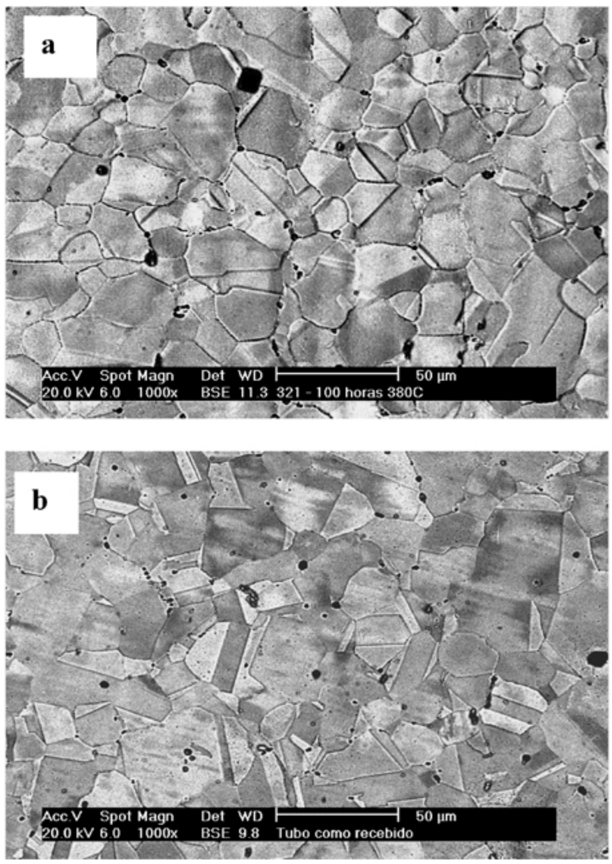

Figure 3 SEM micrograph of a ASTM A312 TP321 sample heat treated at (a) 380°C for 100 h and (b) as-received.

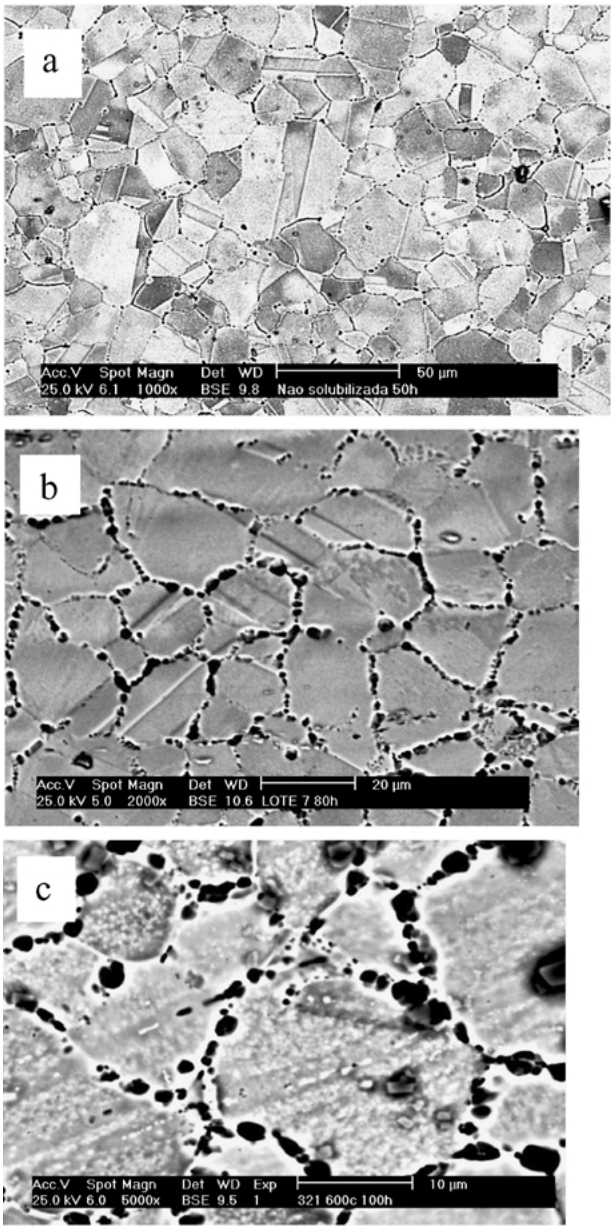

Figure 4 SEM micrograph of a ASTM A312 TP321 sample heat treated at 600°C for (a) 50 h, (b) 80 h and (c) 100 h in an air furnace atmosphere.

2.3. Metallographic etchings

Metallographic etching according to ASTM A-262 was performed. Photomicrographs were acquired using a Zeiss optical microscope and a Philips XL-30 scanning electron microscope (SEM). The microstructures obtained were classified into three types: "step" structure with no ditches at grain boundaries; "dual" structure, with some ditches at grain boundaries; and, "ditch" structure, with one or more grains completely surrounded by ditches. The chemical characterization was carried out using a Link Analytical QX-2000 X-ray dispersive energy analyzer (EDX) attached to the SEM apparatus.

3. Results and discussion

Fig. 2 shows the microstructure of the tube presented in Fig. 1. The sample was taken far from the cracked region. Observation reveals that the grains are completely surrounded by chromium carbides. According to ASTM A 262, this microstructure can be classified as "ditch". It is inferred from this analysis that sensitization makes the tube susceptible to intergranular stress corrosion cracking after a period of exposure to a polythionic acid environment [9, 10].

Under normal operational conditions in a petroleum refining plant, the ASTM A 312 TP321 tubes operate at a temperature range between 350°C and 380°C. Fig. 3 shows the microstructure of a sample heat treated at 380°C for 100 h (Fig. 3a) and another of as-received sample, for comparison (Fig. 3b). The samples have similar microstructures, with no evidence of sensitization at the operational temperature. Thus, these SEM micrographs are evidence that the ASTM A312 TP321 steel pipes are appropriate for use at the operational temperature range of a petroleum refining plant.

Fig. 4 presents the SEM micrographs of samples heat treated at 600°C for 50 h, 80 h and 100 h, showing that all the samples contain chromium carbide precipitates around the grains and the intensity of this chromium carbide precipitation increases with the exposure time. This suggests an increase in the sensitization process as the time of the heat treatment increases. According to ASTM A 262, the microstructure changes first from "step," in samples heat treated for 50 h, to "dual," in those heat treated for 60 h and 70 h, and finally to "ditch" in samples heat treated for longer periods of time.

Fig. 5 shows an EDX spectrum from a region grain boundary in a sample exposed to 600°C for 100 hours, showing a high carbon peak and a low chromium peak, indicating a region poor in chromium and rich in carbon, suggesting that the region has been sensitized.

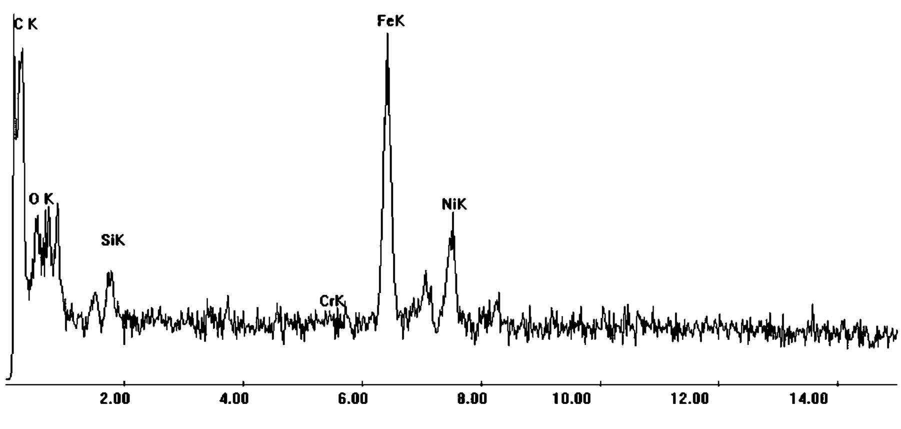

Figure 5 EDX spectrum from a grain boundary region of a sample exposed to 600°C for 100 h.

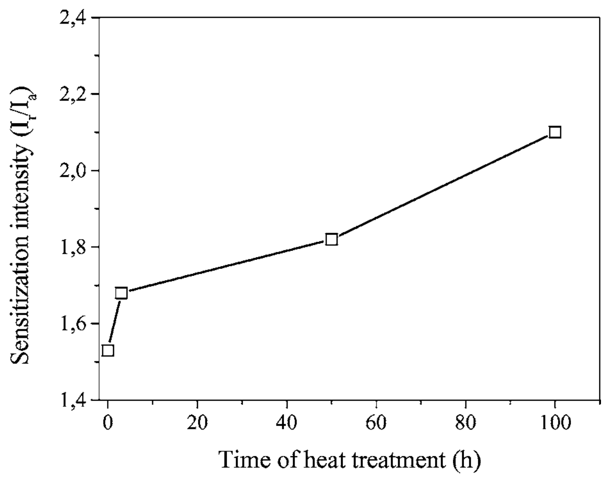

Figure 6 Variation in the sensitization intensity of ASTM A312 TP321 stainless steel after heat treatment in an air furnace atmosphere at 600°C for different exposure periods.

The results derived from DLEPR test on AISI 321 SS samples heat treated at 600°C over different times are presented in Fig. 6, which shows increasing values of the sensitization intensity with heat treatment time in accordance with the SEM observations.

The next step in this work was to investigate what the solution annealing temperature should be in order to reduce sensitization in samples exposed to 600°C for 100 h. Samples were solution annealed at temperatures of 900°C, 950°C, 100°C and 1050°C before being exposed to 600°C for 100 h. Fig. 7 shows the microstructure of these samples. It can be observed that the higher the solution temperature the higher the sensitization intensity. Figs 7a and 7b present a "dual" microstructure where no grains are completely surrounded by carbides, while Figs 7c and 7d present "ditch" microstructures with grains completely surrounded by carbides.

Fig. 8 shows that the sensitization intensity increases with solution annealing temperature in accordance with the SEM observations.

The increase in the sensitization intensity with the increase in the annealing temperature can be explained by a decrease in the combination of carbon with titanium with annealing temperature. The solution annealing treatment at higher temperatures has probably dissolved more carbon that was combined with titanium than one heat treated at lower temperatures. Exposure at 600°C, after solution annealing treatment, precipitated chromium carbide forming regions depleted of chromium along the grain boundaries. Samples solution annealed at 900°C and 950°C before being exposed to 600°C presented a less severe carbide precipitation probably because, at this temperature, it was not possible to dissolve titanium carbides and at the operation temperature there was less carbon present in the matrix.

This analysis is in close agreement with Padilha *et al.* [3] who showed that, after solution annealing, only part of the carbon combines with Ti and the rest of them remains in solution. They also observed that, for operation temperatures around 600°C, the kinetic of chromium carbide formation is more favorable than that of titanium carbide. Above this temperature the opposite holds. Wolynec and Teodoro [11] also observed this behavior in an AISI 347 SS stabilized by niobium.

The solution annealing at 900°C proved to be the most effective at avoiding sensitization during the operation at 600°C. This heat treatment was also efficient when applied to a sample of the cracked tube shown in Fig. 1.

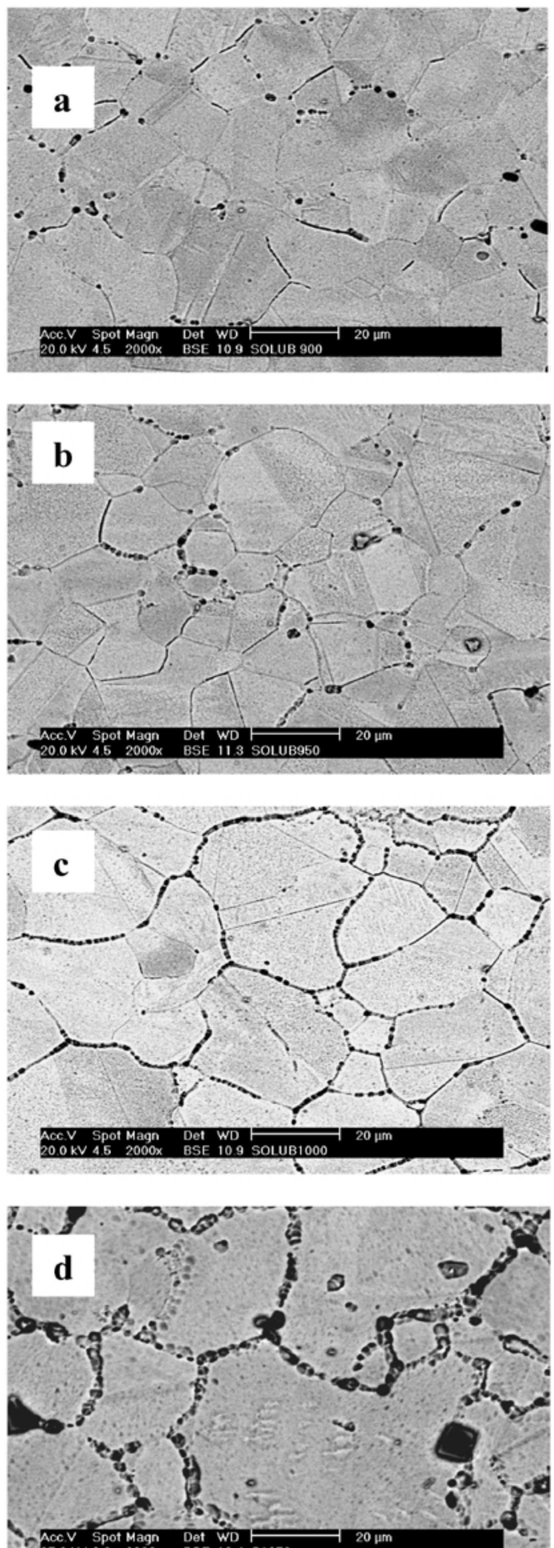

Figure 7 Microstructure of the ASTM A312 TP321 stainless steel after 100 h solution annealing at (a) 900°C, (b) 950°C, (c) 1000°C, (d) 1050°C in an air furnace atmosphere.

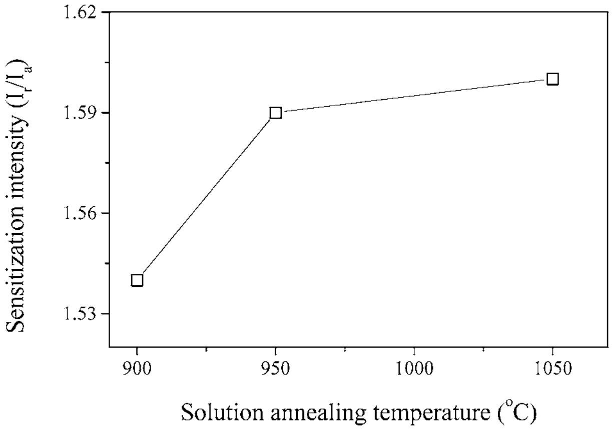

Figure 8 Variation in the sensitization intensity of ASTM A312 TP321 stainless steel solution annealed at different temperatures in an air furnace atmosphere and exposure at 600°C for 100 h.

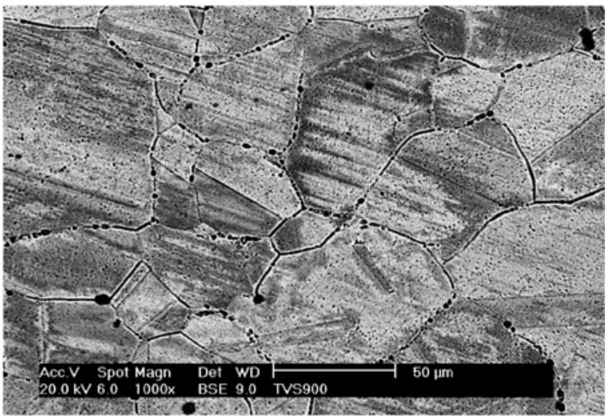

Figure 9 SEM micrograph of a sample of ASTM A312 TP321 stainless steel after one year of operation in a refining plant submitted to solution annealing at 900°C followed by a heat treatment at 600°C for 100 h.

Fig. 9 shows the SEM micrograph of the cracked sample presented in Fig. 1, submitted to the annealing solution at 900°C for 75 min followed by a heat treatment at 600°C for 100 h. The presence of chromium carbide in some localized regions indicates that the annealing solution was effective and has minimized the sensitization intensity.

4. Conclusions

The main conclusions of this study are:

1. Exposure of ASTM A312 TP321 steel pipes to the operation temperature does not cause precipitation of carbides along grain boundaries.
2. The exposure of ASTM A312 TP321 steel pipes at 600°C for 80 hours in the condition "as received" causes severe precipitation of chromium carbides along the grain boundaries characterizing the sensitization of the material despite being a titanium stabilized material.
3. The solution annealing at 900°C was the best heat treatment in order to prevent sensitization at 600°C. This method also works with pipes that were sensitized after one year of operation in a refining plant.

Acknowledgments

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References

1. A. J. SEDRIKS, Corrosion of Stainless Steel (John Willey & Sons Inc, New York, 1996).
2. L. GARVERICK (ed.), Corrosion in the Petrochemical Industry, ASM International, United States, 1994.
3. A. F. PADILHA, G. SCHANZ and K. ANDERKO, *Journal of Nuclear Materials* **105** (1982) 77.
4. P. ZÁHUMENSKÝ, S. TULEJA, J. ORSZÁGOVÁ, J. JANOVEC and V. SILÁDIOVÁ, *Corr. Sci.* **41** (1999) 1305.
5. W. L. CLARKE, R. L. COWAN and W. L. WALKER, Comparative Methods for Measuring Degree of Sensitization in Stainless Steel, Intergranular Corrosion of Stainless Steel, ASTM STP 659, edited by R. F. Steigerwald (ASTM, Philadelphia, Pensylvania, 1978) p. 99.
6. M. AKASHI, T. KAWARNOTO, F. UMEMURA and B. GIJUTSU, *Corros. Engr.* **29** (1980) 163.
7. A. Z. MAJIDI and M. A. STREICHER, *Corrosion* **40** (1984) 584.
8. N. LOPES, M. CID, M. PUIGGALI, I. AZKARE and A. PELAYO, *Matter. Sci. Eng.* **A229** (1997) 123.
9. S. AHMAD, M. L. MEHTA, S. K. SARAF and I. P. SARASWAT, *Corrosion* **41** (1985) 363.
10. P. M. SINGH and S. N. MALHOTRA, *ibid.* **43** (1987) 26.
11. C. A. TEODORO and S. WOLYNEC, *ibid.* **54** (1998) 121.

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