Intergranular Corrosion in a Super-Martensitic Stainless Steel Containing 0.06N-0.025Nb-0.1V

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Introduction

Intergranular corrosion is generally caused by depletion of chromium around grain boundaries, also called sensitization. The lower concentration in chromium is a consequence of chromium carbide formation in grain boundaries, caused by heat treatments in specific temperature ranges and/or by welding. In the literature is possible to find plenty of information regarding intergranular corrosion in austenitic and ferritic stainless steels, ASTM A262A[1] and A763W[2] describe electrolytic tests in oxalic acid to detect rich chromium phases, but those techniques do not supply quantitative results. It is also possible to determine the susceptibility of such steels to intergranular corrosion based in the electrochemical potentiokinetic reactivation technique (EPR), which presents three different versions: single loop, double loop and simplified cycle[3]. Nowadays the standard ASTM G 108[4], is also available to test intergranular corrosion in austenitic stainless steels 304 and 304L (UNS S30400 and UNS S30403) in a solution of 0,5M H2SO4+0,01M KSCN.
Although the use of EPR techniques is not a standardized method to test intergranular corrosion resistance in ferritic and martensitic stainless steels it is possible to find some results in the literature such as the study made by Serna[5] on the ferritic stainless steel UNS S43000, through the DL-EPR technique in 0,5M H_2SO_4 measurements were made in isothermal treated samples in the range from 500°C to 600°C from 5 minutes to 16 hours. In the study, two maximum intergranular corrosion susceptibility peaks were reported as a function of the heat treatment time. Magri[6] investigated the intergranular corrosion of the martensitic stainless steel UNS S41000 through the use of DL-EPR technique in 1M H_2SO_4 solution, in tempering temperatures from 300 to 700°C, reporting that maximum susceptibility to intergranular corrosion was found in the tempering temperature of 550°C.
In the present work the DL-EPR technique has been used to detect intergarnular corrosion in a super-martensitic stainless steel (13Cr5Ni1Mo_0,06N_0,025Nb_0,1V). The study has been made in samples austenitized at 1050°C and then tempered at 400°C, 500°C, 600°C and 700°C utilizing several electrolytic solutions (XM H_2SO_4 + YM KSCN).

Experimental

Hot rolled super-martensitic stainless steel plates (12mm) have been used in the study, chemical composition is given in Table 1.

Table 1.Chemical Composition.

Steel	C	Cr	Ni	Mo	N	Nb	V	Ti	Al
13Cr5Ni1Mo_0,06N_0,025Nb_0,1V	0,03	12,8	5,26	0,94	0,05	0,025	0,09	0,01	0,03

The material has been supplied by McMaster and China North Eastern University. The plates have been cut into 10mm cubes and austenitized at 1050°C for 30 minutes, oil cooled and then tempered at 400°C, 500°C, 600°C and 700°C (air cooled). Test using DL-EPR technique have been made with scanning speed of 1.67 mV/s, starting from the corrosion potential until 500mV (ascendant) and then reverted until the corrosion potential again. Since there is no standard about the use of DL-EPR technique in super martensitic stainless steels, six different electrolytic solutions were tested in order to determine the most adequate in this investigation. The electrolytes used were: 0.5M H2SO4; 1M H2SO4; 1.5M H2SO4, 0.5M H2SO4+0.01M KSCN; 1M H2SO4+0.005M KSCN and 0.5M H2SO4+0.005M KSCN.

The resulting DL-EPR curves supply two maximum current peaks: activation current (Ia) and reactivation current (Ir), through the ratio Ir/Ia the sensitization level – degree of sensitization (DOS) was determined.

Results and Discussion

Solutions without KSCN were less aggressive and therefore did not presented the reactivation current (Ir=0). Table 2 gives the average DOS values for the three solutions containing KSCN.

Table 2.Average DOS values for steel 13Cr5Ni1Mo_0,06N_0,025Nb_0,1V. Minimum of three tests per condition studied

	Tempering temperature			
Electrolyte Solution	400°C	500°C	600°C	700°C
0.5M H_2SO_4+0.01M KSCN	0	0.42	0.56	0.55
1.0M H_2SO_4+0.005M KSCN	0	0.49	0.74	0.55
0.5M H_2SO_4+0.005M KSCN	0	0.35	0.45	0.22

After DL-EPR tests optical microscope examination reveal remarkable differences related to intergranular corrosion resistance among the different heat treatments. Figure 1 shows the surface and DL-EPR curves for tempering conditions at 600°C and 700°C.

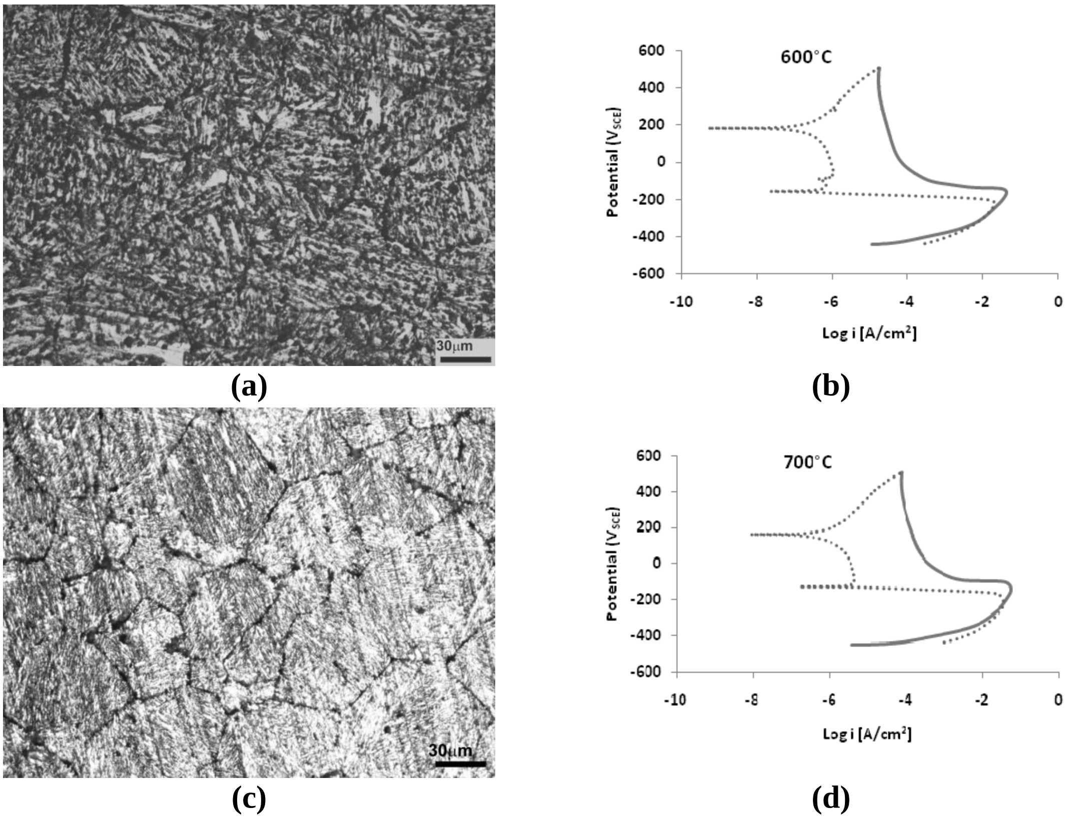

Figure 1. Optical micrograph of specimens surface and Log (current density) vs. potential curves obtained by DL-EPR test for different heat treatment conditions in 0,5M H2SO4+0,01M KSCN solution: (a, b) tempered at 600°C; (c, d) tempered at 700°C.

Figure 2 presents DOS as a function of the heat treatments in the three solutions containing KSCN.

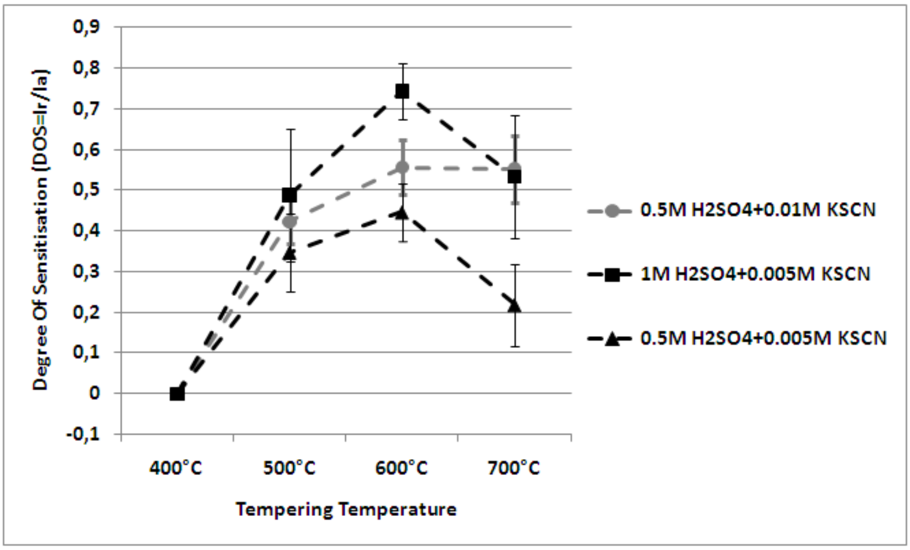

Figure 2. DS as a function of tempering temperature for the three solutions containing KSCN.

The electrolytic solutions containing H_2SO_4 (without KSCN) did not present reactivation peak current (Ir). Therefore, these DOS values were not presented. It is concluded that such solutions are not adequate for the DL-EPR study of intergranular corrosion in the super martensitic stainless steel 13Cr5Ni1Mo_0,06N_0,025Nb_0,1V ".
The electrolytic solutions 0,5M H2SO4+0,005M KSCN and 1M H2SO4+0,005M KSCN give satisfactory results because DOS values can be distinguished for each heat treatment condition, however, it can be noted that the standard deviations in 0,5M H2SO4+0,005M KSCN solution are smaller (Figure 2).
The tempering condition at 600°C presented the higher DOS value. At the same time, the condition at 400°C showed null DOS in all conditions studied.

Acknowledgements
The authors acknowledge CNPq (Council for Scientific and Technological Development/Brazil) under Project #140108/2012-2, and CBMM (Companhia Brasileira de Metalurgia e Mineração) for financial support.

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