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Susceptibility to Stress Corrosion Cracking of 254SMO SS

Lorenzo De Micheli[a]*, *Silvia Maria Leite Agostinho*[a], *Giordano Trabanelli*[b], *Fabrizio Zucchi*[b]

[a]*Institute of Chemistry of the University of São Paulo 05508-900 São Paulo - SP, Brazil,*
[b]*Corrosion Study Center "A. Daccò", Department of Chemistry, University of Ferrara, Italy*

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The susceptibility to stress corrosion cracking (SCC) of solubilized and sensitized 254SMO SS was studied in sodium chloride, and sodium fluoride solutions at 80 °C and sulfuric acid solutions in presence of sodium chloride at 25 °C. The influence of salt concentration, pH values and the addition of thiosulfate was examined. The susceptibility to SCC was evaluated by Slow Strain Rate Tests (SSRT), at $1.5 \times 10^{-6}\ s^{-1}$ strain rate. The behavior of 254SMO was compared to those of AISI 316L SS and Hastelloy C276.

254SMO showed an excellent resistance to SCC in all conditions, except in the more acidic solutions (pH ≤ 1) where, in the sensitized conditions, intergranular stress corrosion cracking occurred.

Keywords: *stainless steel, stress corrosion cracking, chloride and fluoride*

1. Introduction

The 254SMO[1] (UNS S31254) is a stainless steel that contains higher quantities of chromium, nickel, molybdenum and nitrogen than common stainless steels, such as 316, 316L and 304. The synergetic effect of those alloy elements promotes a higher corrosion resistance in chloride media[1,2]. The 254SMO was developed twenty years ago but there are not many studies on its performance in different media[3-11]. Olsson[10,11] presents the 254SMO as a material with excellent resistance to corrosion in halide solutions. Qvarfort[5] determined its critical pitting temperature to be about 89 °C in 5 M NaCl aqueous solutions. De Micheli showed the corrosion resistance of 254SMO in hydrochloric[12] and phosphoric[3] acid media.

Stress corrosion cracking (SCC) is a result of synergic interaction of mechanical tension and chemical reaction. Nickel alloys, stainless steels (SS), aluminum alloys and other metallic alloys are susceptible to SCC[13].

The alloy composition and structure influence the SCC susceptibility[13-14]. Well *et al.*[15] showed the importance of applied potential to SCC for 304 SS in thiosulphate media. Zucchi *et al.*[16-17] studied the applied potential, fluoride and chloride concentration, the temperature and pH influence on intergranular stress corrosion cracking (IGSCC) for 304 SS. Nishimura[18] showed the influence of pH on IGSCC of UNS S30400 and UNS S31600 in hydrochloric acid media. Ashour *et al.*[19] studied the influence of thiosulfate on SCC of UNS S31600.

The aim of the present work was to study the susceptibility of 254SMO alloy to stress corrosion cracking (SCC) and to compare it with that observed in 316L stainless steel (UNS S31603) and Hastelloy C276 (UNS S10276). The 316L stainless steel and Hastelloy C276 were chosen for this comparative study because a recent study has shown that, in acid media, 254SMO has better resistance than 316L and almost the same behavior of Hastelloy C276[3,7,12].

2. Experimental

Table 1 presents the chemical composition of tested alloys. The specimens for SCC tests had a 17 mm length and 4 mm in diameter gauge. The surface of the specimens was prepared by treatment with emery paper up to 600 grit, rinsed with water, degreased with acetone and air-dried. The tested alloys were thermally treated under two conditions: solubilized (1150 °C for 1 h and water cooled); sensitized (871 °C for 5 h and air cooled). This treatment was based on TTT curves (temperature-time-transforma-

*e-mail: ldmicheli@hotmail.com
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Table 1. Chemical composition of the studied material in mass percent.

	254 SMO UNS S31254	316L UNS S31603	Hastelloy C276 UNS S10276
C	0.02	0.02	0.01
Si	0.42	0.50	0.09
Mn	0.49	1.71	0.28
Cr	20.1	16.2	16.0
Ni	18.4	11.0	balance
Mo	6.42	2.18	15.5
Cu	0.77	0.35	0.01
N	0.21	0.07	
P	0.02	0.03	0.01
V			0.25
S	0.004	0.023	0.015
W			3.67
Fe	balance	balance	6.32

tion). The conditions chosen were the best way to sensitize the materials.

The test solutions, prepared from analytical grade reagents and distilled water, were: 1 and 3 mol/L sodium chloride at pH 6, 3, 2, 1; 0.5 and 1 mol/L sodium fluoride; 3 mol/L sodium chloride + 0.1 mol/L sodium thiosulphate at pH 6, 4 and 3; 5 mol/L sulfuric acid + 1 mol/L sodium chloride. In the presence of thiosulfate the solutions were deaerated by nitrogen bubbling. The experiments were conducted at 25 °C, 70 °C and 80 °C. Zucchi[4-5] studying 304 SS observed a more aggressive attack by fluoride than chloride in SCC. The sulfidric acid is an aggressive media and the thiosulphate presents similar behavior of sulfidric acid in relation to SCC[7]. The thiosulfate was chosen due to operation facilities.

The Slow Strain Rate Tests (SSRT) were performed with a strain rate of $1.5 \times 10^{-6}\ s^{-1}$ at open corrosion potential. Each material has the best strain rate that must be measured. Early studies showed that for this material the best strain rate is around $10^{-6}\ s^{-1}$. At the end of the tests the specimens were examined with a binocular microscope and a SEM in a few cases in order to identify the morphology of the crack.

Anodic polarization curves were recorded, with a scan rate of 0.1 mV/s, on the three alloy electrodes in the different solutions, by using an Ag/AgCl reference electrode.

3. Results and Discussion

Susceptibility to SCC was evaluated using the ratio between percentage elongation to failure in aggressive medium (ε_A) and in inert environment (ε_I), such as air or inert solution.

In Fig. 1 the sensitized 254 SMO stress/% elongation curves, in 3 mol/L sodium chloride solutions at different pH values are shown. Table 2 reports the ratio ($\varepsilon_A/\varepsilon_I$) values of solubilized and sensitized 254 SMO obtained in the different solutions. Table 2 reports also the pitting potential values determined by the anodic polarization curves.

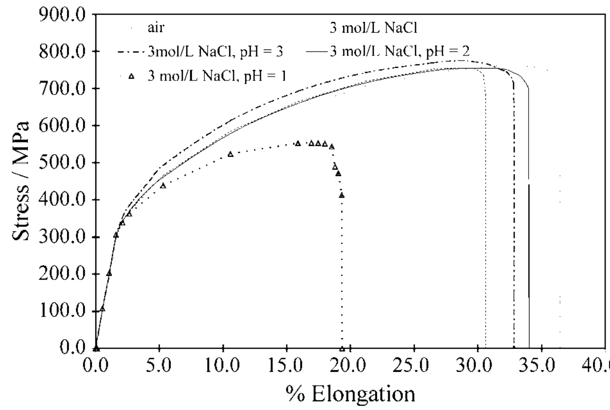

Figure 1. Stress / % elongation curves for a sensitized 254 SMO in 3 mol/L NaCl as function of pH at 80 °C.

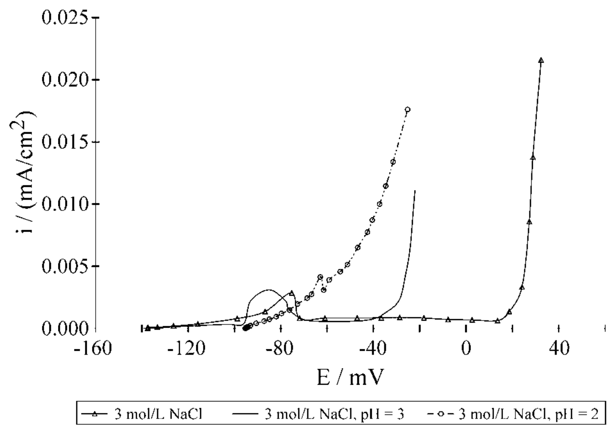

Figure 2. Potentiodynamic polarization curves (0.1 mV/s) for 254 SMO in NaCl solutions at 80 °C.

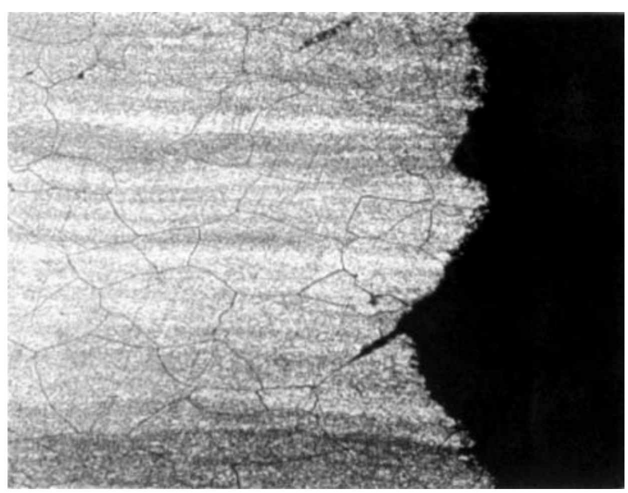

Figure 3. Scanning electron micrographs, as polished and with oxalic acid attack, for 254 SMO solubilized after SSRT (80 x).

The increase of chloride concentration from 1 to 3 mol/L or the decrease of pH values from 6 to 2 in 3 mol/L sodium chloride solutions did not change the ratio ($\varepsilon_A/\varepsilon_I$) values in significative manner. If we consider that in the literature[20] a ratio ($\varepsilon_A/\varepsilon_I$) value of 0.8 or higher is considered an index of immunity to SCC, it is possible to affirm that the sensitized 254 SMO does not suffer SCC in sodium chloride solution up to 3 mol/L, pH > 2, at 80°C.

Conversely in 3 mol/L sodium chloride solutions at pH 1 the ratio ($\varepsilon_A/\varepsilon_I$) of sensitized 254 SMO was 0.54, whereas the solubilized steel showed a ratio ($\varepsilon_A/\varepsilon_I$) equal to 0.86.

SEM observation of the fracture surface of solubilized and sensitized 254SMO, in 3 mol/L sodium chloride at pH 1, showed that in solubilized conditions the fracture was essentially ductile and only a very narrow zone presented transgranular crack (Fig. 6). The sensitized 254 SMO showed a significative cracking transgranular (Fig. 7). The intergranular attack was emphasized because the rupture happened during the night and the specimen remained immersed until next morning.

The pitting potential values of sensitized 254 SMO decreased regularly by increasing the chloride concentration and by decreasing the pH value in 3 mol/L sodium chloride solutions. At pH 1 254SMO was in active state. It was observed from SSRT a reduction of the section area by the chemical attack. The same steel only immersed for the same time in this solution results a less intensive corrosion. Thus there was a synergistic corrosion (chemical/tension) in this media.

It must be notice that the sensitization treatment provoked a noticeable modification on the mechanical characteristics of 254 SMO. In Table 3 the % elongation to fracture of the solubilized and sensitized 254 SMO in different solutions are compared. In any case the ductility of sensitized 254 SMO was hardly decreased. In 1 mol/L sodium chloride in which no SCC was observed the % elongation to fracture decreased from 56.5% in the solubilized to 32.9% in the sensitized 254 SMO. This last material showed a high ultimate strength resistance, suggesting a hardening due to the precipitation of new phases at grain boundaries. The sensitization treatment produced a transition from the ductile transgranular fracture of solubilized to the transgranular fracture of sensitized material, as Figs. 3, 4, 5 show.

Zucchi[16-17] *et al.* observed that fluoride anions were more aggressive than chloride to sensitized 304 stainless steel. The results of SSRT in sodium fluoride solutions on sensitized 254SMO showed that also in 1 mol/L sodium fluoride sensitized 254 SMO was immune to SCC (Table 2). The pitting potential values of 254 SMO in sodium fluoride resulted higher than those in sodium chloride,

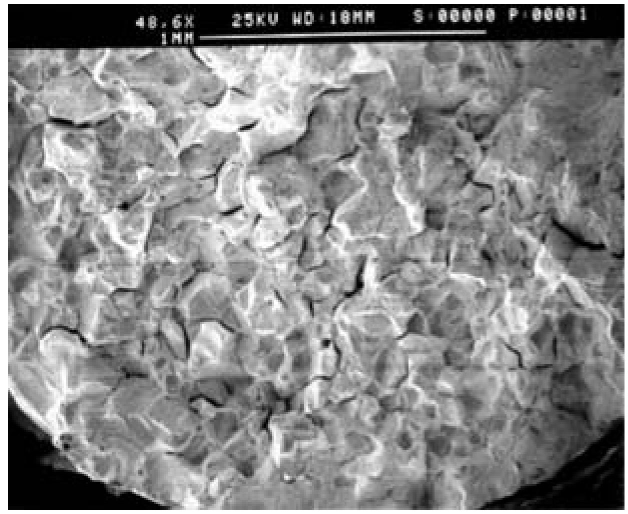

Figure 4. Scanning electron micrographs for 254 SMO sensitized, after SSRT in 1mol/L NaCl solution at 80 °C.

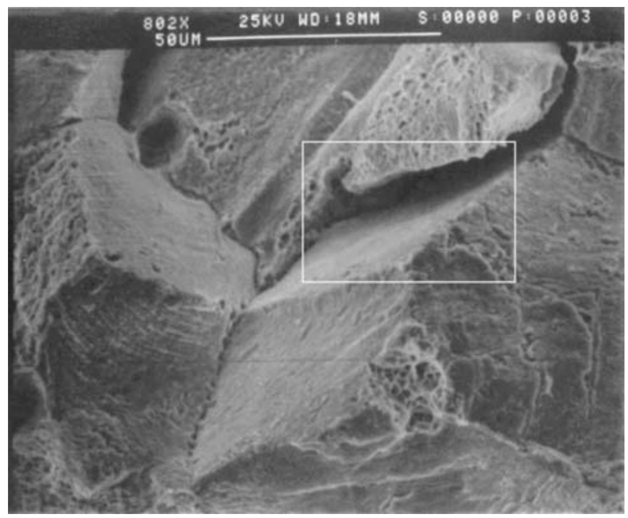

Figure 5. Scanning electron micrographs for 254 SMO sensitized, after SSRT in 1mol/L NaCl solution at 80 °C.

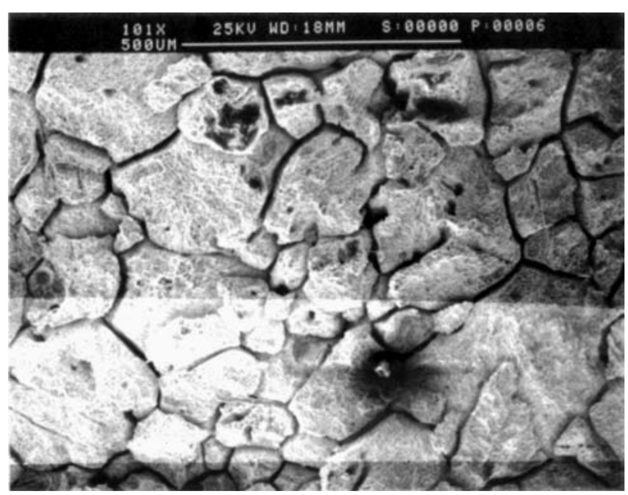

Figure 6. Scanning electron micrographs for 254 SMO sensitized, after SSRT in 3mol/L NaCl, pH = 1 solution at 80 °C.

Table 2. $\varepsilon_A/\varepsilon_I$ values, pitting potential (Ep) and the resistance for 254 SMO in solution at 80°C.

	Solubilized steel			Sensitized steel		
	($\varepsilon_A/\varepsilon_I$)	Ep	MPa	($\varepsilon_A/\varepsilon_I$)	Ep	MPa
0.5 mol/L NaCl		315			150	
1 mol/L NaCl (70 °C)		1000				
1 mol/L NaCl		100		0.90	120	756
3 mol/L NaCl		100		0.84	20	771
3 mol/L NaCl, pH = 3				0.90	-30	771
3 mol/L NaCl, pH = 2		100		0.93	-60	761
3 mol/L NaCl, pH = 1	0.86	Generalized corrosion	518	0.54	Generalized corrosion	551
0.1 mol/L NaF				0.94	350	751
1 mol/L NaF (80 °C)		320		0.91	350	744
3 mol/L NaCl /0.1 mol/L $Na_2S_2O_3$ *		210		0.74	-120	800
3 mol/L NaCl /0.1 mol/L $Na_2S_2O_3$, pH = 4*	0.88	160	671	0.72		799
3 mol/L NaCl /0.1 mol/L $Na_2S_2O_3$, pH = 3*		90		0.72	-250	800
5 mol/L H_2SO_4 / 1 mol/L NaCl (25 °C)	0.89	Generalized corrosion	697	0.66	Generalized corrosion	755

*Without oxygen by nitrogen bubbling.

showing that this alloy was very resistant to localized corrosion (pitting and SCC) in fluoride media.

254 SMO was also tested in 3 mol/L sodium chloride solution in the presence of thiosulfate. In fact it is known that the addition of thiosulfate to sodium chloride solutions stimulates the pitting corrosion[21-22] and provokes SCC on different alloys. The addition of 0.1 mol/L thiosulfate to 3 mol/L sodium chloride shifted the pitting potential of sensitized 254 SMO towards negative potentials (-250 mV at pH 3). SSRT indicated that sensitized 254 SMO was susceptible to SCC in this environment. Numerous transgranular cracks were present on the gauge section. Figure 8 shows the apex of one of these cracks. Solubilized 254 SMO did not present susceptibility to SCC in this environment.

Sensitized 254 SMO was also susceptible to SCC in 5 mol/L sulfuric acid plus 1 mol/L sodium chloride, at 25 °C. The polarization curves showed that the steel was active in this solution. The morphology of the cracks was intergranular (Fig. 10). The influence of stress was evidenced by testing sensitized 254 SMO specimens without

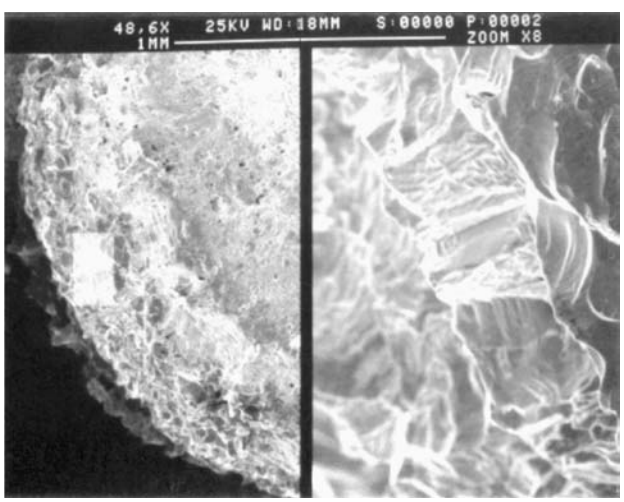

Figure 7. Scanning electron micrographs for 254 SMO solubilized, after SSRT in 3mol/L NaCl, pH = 1 solution at 80 °C.

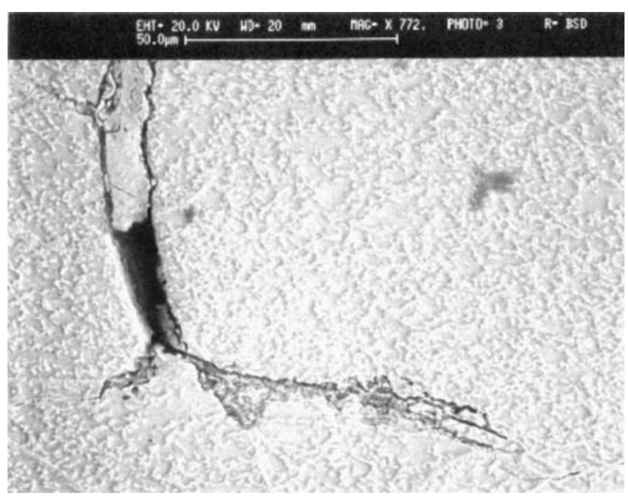

Figure 8. Scanning electron micrographs, polished, with oxalic acid attack, for 254 SMO sensitized after SSRT, in 3 mol/L NaCl / 0.1 mol/L $Na_2S_2O_3$, pH = 4 at 80 °C.

Table 3. Maximum elongation values (%) for 254 SMO.

	Maximum elongation values (%)			
	1 mol/L NaCl (80 °C)	2.9 mol/L NaCl 0.1 mol/L HCl (80 °C)	3 mol/L NaCl 0.1mol/L $Na_2S_2O_3$ pH = 4 (80 °C)	5 mol/L H_2SO_4 1 mol/L NaCl (25 °C)
UNS S31254 solubilized	56.5	48.4	49.5	50.4
UNS S31254 sensitized	32.9	19.7	26.2	23.9

any external tension in the same solution, for 68 h (fracture time to SSRT). The specimens at the end of the test were corroded, but the examination of the section with metallographic microscope did not evidence any intergranular attack (Fig. 10).

Table 4 reports the results of SSRT performed on Hastelloy C276. The tests were carried out in the more aggressive solutions due to the known high resistance to SCC of this material. Hastelloy C276 showed a remarkable susceptibility to SCC in 3 mol/L sodium chloride at pH = 1 in sensitized condition. Numerous intergranular cracks were evident on the specimens after SSRT (Fig. 11). On the other hand, solubilized Hastelloy C276 did not present SCC in this aggressive medium.

Hastelloy C276 was not susceptible to SCC in 3 mol/L sodium chloride in the presence of thiosulfate.

The examination by SEM of the sensitized Hastelloy C276, tested in 5 mol/L sulfuric acid + 1 mol/L sodium chloride showed the presence of some intergranular cracks,

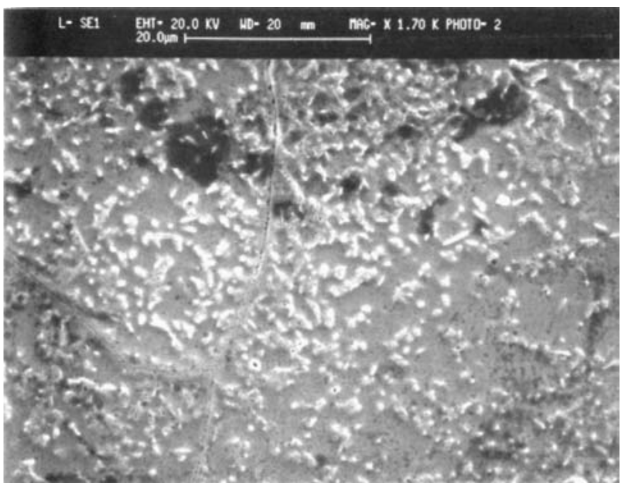

Figure 9. Scanning electron micrographs, polished, with oxalic acid attack, for 254 SMO sensitized after SSRT, in 3 mol/L NaCl / 0.1 mol/L $Na_2S_2O_3$, pH = 4 at 80 °C.

Figure 10. Scanning electron micrographs for 254 SMO sensitized, after SSRT in 5 mol/L H_2SO_4 / 1 mol/L NaCl solution at 25 °C.

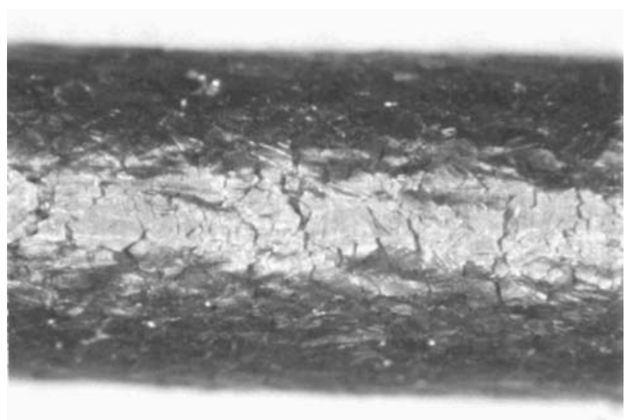

Figure 11. Lateral surface of UNS S10276 electrode after SSRT in 5 mol/L H_2S0_4 / 1 mol/L NaCl at 25 °C.

Figure 12. Scanning electron micrographs for sensitized UNS S10276, after SSRT in 2.9 mol/L NaCl / 0.1 mol/L HCl at 80 °C.

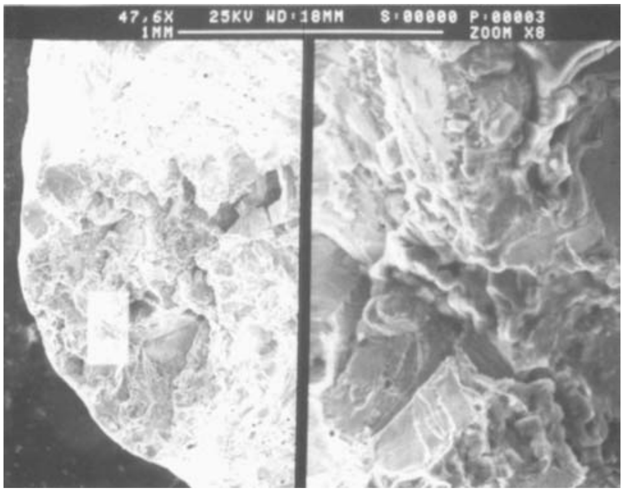

Figure 13. Scanning electron micrographs for 316L sensitized, after SSRT in 3 mol/L NaCl, $Na_2S_2O_3$ 0.1 mol/L solution at 80 °C.

Figure 14. Scanning electron micrographs for 316L sensitized, after SSRT in 5 mol/L H_2SO_4 / 1 mol/L NaCl solution at 25 °C.

Table 4. $\varepsilon_A/\varepsilon_I$ values, pitting potential and resistance for Hastelloy C276 in solutions at 80 °C.

	Solubilized		Sensitized		
	$\varepsilon_A/\varepsilon_I$	MPa	$\varepsilon_A/\varepsilon_I$	Ep	MPa
3 mol/L NaCl			0.90	340	811
3 mol/L NaCl, pH = 2			0.90	330	811
3 mol/L NaCl, pH = 1	0.99	706	0.66		695
3 mol/L NaCl / 0.1 mol/L $Na_2S_2O_3$ *			0.93	400	848
3 mol/L NaCl / 0.1 mol/L $Na_2S_2O_3$, pH = 4*			0.93	-50	783
5 mol/L H_2SO_4 / 1 mol/L NaCl (25 °C)			0.90	G.C.	783

*Without oxygen by nitrogen bubbling.
G.C.: generalized corrosion.

Table 5. $\varepsilon_A/\varepsilon_I$ values, pitting potential (Ep) and the resistance for 316L in solution at 80 °C.

	Solubilized		Sensitized		
	$\varepsilon_A/\varepsilon_I$	MPa	$\varepsilon_A/\varepsilon_I$	Ep	MPa
3 mol/L NaCl	0.91	472	0.94	-220	498
3 mol/L NaCl, pH = 2			0.94	-345	495
3 mol/L NaCl, pH = 1			0.68	G.C.	312
0.1 mol/L NaF			0.89	400	495
1 mol/L NaF			0.81	240	471
3 mol/L NaCl / 0.1 mol/L Na_2S_2O3*	0.94	489	0.77	-270	499
5 mol/L H_2SO_4 / 1 mol/L NaCl (25 °C)	0.91	492	0.91	G.C.	502

*Without oxygen by nitrogen bubbling.
G.C.: generalized corrosion.

not more deep (Fig.12), as the ratio ($\varepsilon_A/\varepsilon_I$) value equal to 0.9 confirms.

Hastelloy C276 showed susceptibility to IGSCC, comparable to that of 254 SMO, only in 3 mol/L sodium chloride at pH 1 and a much lower susceptibility in 5 mol/L sulfuric acid + 1 mol/L sodium chloride. Hastelloy C276 was active in these two environments.

Table 5 reports the results of the tests performed on AISI 316L. Solubilized AISI 316L was immune to SCC in 3 mol/L sodium chloride in the absence and in presence of thiosulphate and in 5 mol/L sulfuric acid + 1 mol/L sodium chloride solutions. Sensitized steel, as well as the other two sensitized materials, presented SCC in 3 mol/L sodium chloride pH 1. In this solution the steel was active.

SCC occurred also on sensitized AISI 316L in 3 mol/L sodium chloride in the presence of thiosulfate at pH 3. In this case the cracks had a mixed inter- and transgranular morphology (Fig. 13)

The resistance to SCC of sensitized AISI 316L in 5 mol/L sulfuric acid + 1 mol/L sodium chloride was similar to that of sensitized Hastelloy C276. The ratio ($\varepsilon_A/\varepsilon_I$) value was almost the same (0.91) and only the examination by SEM of the fracture surface evidenced the presence of a not deep zone cracked by SCC (Fig. 14).

4. Conclusions

Sensitized 254 SMO presents susceptibility to IGSCC only in very acidic solutions (3 mol/L sodium chloride pH = 1 at 80 °C and 5 mol/L sulfuric acid + 1 mol/L sodium chloride at 25 °C). However the resistance of this material is comparable to those of sensitized Hastelloy C276 and AISI 316L.

Sensitized Hastelloy C276 shows a better resistance in 3 mol/L sodium chloride + 0.1 mol/L sodium thiosulphate solutions than that observed for sensitized 254SMO and AISI 316L.

The solubilized alloys do not suffer any type of SCC in the tested solutions.

In spite of different pitting and generalized corrosion resistance for 254SMO SS, 316L SS and Hastelloy C276, the stress corrosion cracking resistances are almost equivalent in there studied media.

These three materials have a good resistance to SCC.

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