

# Electrochemical studies of 254SMO stainless steel in comparison with 316L stainless steel and Hastelloy C276 in phosphoric acid media in absence and presence of chloride ions

L. DE MICHELI  
A. H. P. ANDRADE  
C. A. BARBOSA  
S. M. L. AGOSTINHO

*The electrochemical behaviour of 254SMO stainless steel in phosphoric acid media, both with and without chloride ions, has been investigated and compared with that of 316L stainless steel and Hastelloy alloy C276. Open circuit potential measurements, potentiodynamic polarisation curves, and SEM analyses were used in the study. The 254SMO alloy displayed better corrosion resistance than 316L, being passive in 3M H<sub>3</sub>PO<sub>4</sub> solutions for [Cl<sup>-</sup>] ≤ 1M and in 6M H<sub>3</sub>PO<sub>4</sub> solutions for [Cl<sup>-</sup>] ≤ 0.1M. Its performance was comparable with that of Hastelloy C276, except in 6M H<sub>3</sub>PO<sub>4</sub> solutions containing 1M NaCl, where 254SMO exhibited an active region over the entire range of temperatures studied (26–70°C) while Hastelloy C276 remained passive under these circumstances.*

*Dr De Micheli and Dr Agostinho are in the Institute of Chemistry of the University of São Paulo (IQUSP), Av. Prof. Lineu Prestes, 748-B3i, São Paulo, SP, Brazil 05508-900, Dr Andrade is in the Institute of Energetic and Nuclear Research, São Paulo, Brazil, and Eng Barbosa is with Villares Metals SA. Manuscript received 29 October 1996; accepted 1 December 1998.*

© 1999 IoM Communications Ltd.

## INTRODUCTION

Stainless steels are normally resistant to attack in phosphoric acid media. However, the presence of impurities such as chloride and fluoride ions promotes the corrosion of these materials.<sup>1,2</sup>

Avesta Sheffield 254SMO stainless steel (UNS S31254) was developed to provide high corrosion resistance in chloride media where common stainless steels such as 304, 316, and 316L suffer pitting corrosion. The 254SMO alloy has been available since 1977, and there have been a number of studies concerning its resistance to corrosion in different media.<sup>3–9</sup>

The aim of the present work was to study the electrochemical behaviour of 254SMO alloy in phosphoric acid media, in the absence and presence of chloride ions, and to compare it with that of 316L stainless steel (UNS S31603) and Hastelloy C276 (UNS NI 0276). The 316L stainless steel and Hastelloy C276 were chosen for this comparative study because a recent study<sup>5</sup> has shown that, in hydrochloric acid media, 254SMO displays better corrosion resistance than 316L and almost the same behaviour as Hastelloy C276. Open circuit potential measurements, potentiodynamic polarisation curves, and scanning electron microscopy were used in the study.

## EXPERIMENTAL

Table 1 presents the chemical compositions of the materials used, which were cut as disc electrodes with areas of 1.02 cm<sup>2</sup> (254SMO) and 0.48 cm<sup>2</sup> (316L and Hastelloy C276). These electrodes were polished with progressively less coarse emery papers (of 320, 400, and 600 grit), rinsed first with water then with ethanol, and air dried. The

solutions were prepared from analytical grade reagents and doubly distilled water. The experiments were conducted at room temperature (26°C) and at 45, 53, and 70°C. A conventional electrolytic cell was used with a saturated calomel reference electrode (SCE) and a platinum foil counter electrode. Potential measurements were made using a digital voltmeter while a PAR model 273A potentiostat coupled to a 386 microcomputer was used for the determination of polarisation curves. Microscopic analysis was undertaken with a Philips XL-30 scanning electron microscope (SEM).

## RESULTS AND DISCUSSION

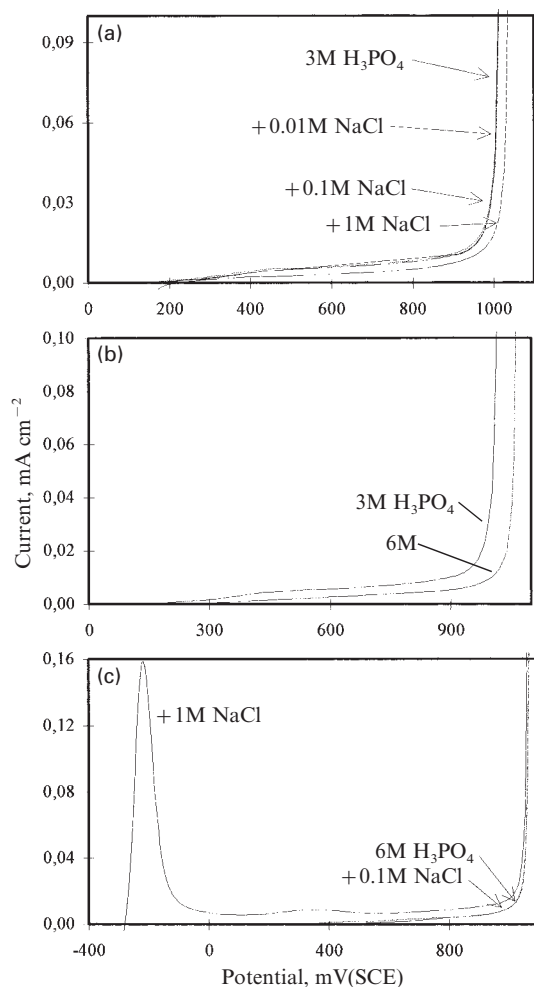
Values of the corrosion potential  $E_{\text{corr}}$  for the alloys in each solution were established from open circuit potential measurements;  $E_{\text{corr}}$  was considered to have been attained when the potential drift became less than 1 mV in 10 min. The  $E_{\text{corr}}$  values determined for the three alloys in each of the seven solutions used in the investigation after 16 h immersion at ambient temperature are given in Table 2.

From Table 2 it can be seen that for the 254SMO alloy the values of  $E_{\text{corr}}$  are approximately 180 and 260 mV(SCE) in chloride free solutions of 3 and 6M phosphoric acid respectively. The presence of chloride ions shifts  $E_{\text{corr}}$  to more positive values, except in 6M H<sub>3</sub>PO<sub>4</sub> solutions where the addition of 1M NaCl moves  $E_{\text{corr}}$  by more than 500 mV in the negative direction to a potential of approximately –284 mV(SCE), suggesting that the metal surface is in an active state.

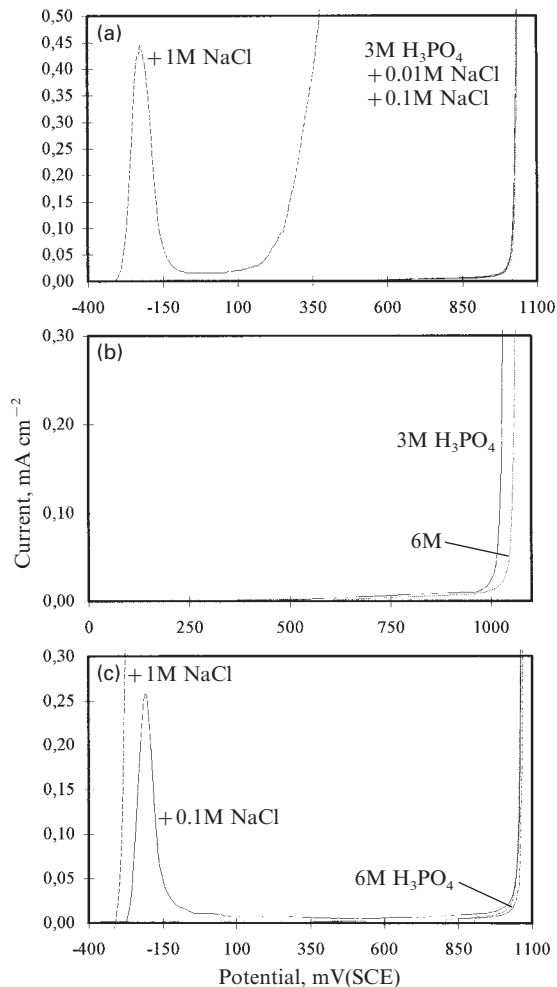
In the case of 316L stainless steel, negative values for  $E_{\text{corr}}$  are encountered more frequently in the presence of chloride ions. For example, the addition of 1M NaCl

Table 1 Chemical compositions of alloys studied, wt-%

	C	Si	Mn	Cr	Ni	Mo	Cu	N	P	S	Fe
254SMO	0.02	0.42	0.49	20.1	18.4	6.42	0.77	0.21	0.02	0.004	Bal.
316L	0.02	0.50	1.71	16.2	11.0	2.18	0.35	0.07	0.03	0.023	Bal.
Hastelloy C276	...	...	...	15.0	Bal.	16.0	6.0	...	...	...	6.0



1 Potentiodynamic polarisation curves for 254SMO stainless steel in given  $H_3PO_4$  solutions at 26°C: scan rate  $0.5 \text{ mV s}^{-1}$



2 Potentiodynamic polarisation curves for 316L stainless steel in given  $H_3PO_4$  solutions at 26°C: scan rate  $0.5 \text{ mV s}^{-1}$

to 3M  $H_3PO_4$  solution or of 0.1M NaCl to 6M  $H_3PO_4$  solution is sufficient to shift  $E_{\text{corr}}$  values to negative potentials. For Hastelloy C276, however, all  $E_{\text{corr}}$  values are positive, suggesting that a passive state exists in all the media studied.

Figure 1a shows the electrochemical behaviour of 254SMO in 3M  $H_3PO_4$  in the absence and presence of chloride ions at room temperature. It can be observed that the presence of 1M NaCl decreases the passive current value and shifts the transpassivation potential  $E_{\text{trans}}$  in the positive direction. In the presence of 6M  $H_3PO_4$  the passive current density decreases and the value of  $E_{\text{trans}}$  becomes more positive, for each of the three materials studied, when compared with their behaviour in 3M  $H_3PO_4$ , as can be seen for 254SMO in Fig. 1b. This change in potential can be attributed to variations in solution pH and to the fact

that the 6M  $H_3PO_4$  solutions have a larger passivating effect than the 3M  $H_3PO_4$  solutions, as can be seen from the decrease in current density values as the  $H_3PO_4$  concentration increases.

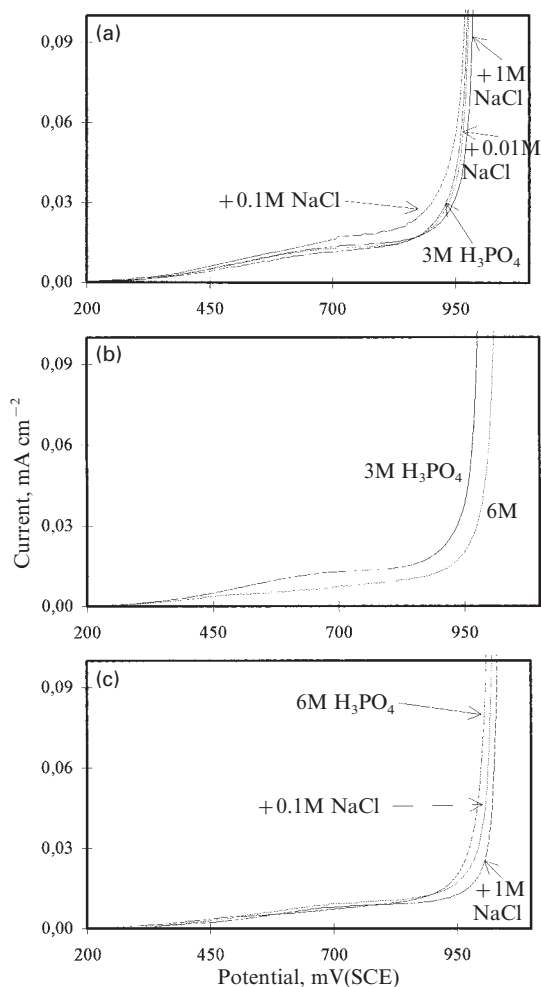
For 254SMO in 6M  $H_3PO_4$  (Fig. 1c) the presence of 0.1M NaCl does not change the polarisation curves, but with 1M NaCl there is an active region with a critical current density equal to  $0.16 \text{ mA cm}^{-2}$  and a critical potential at  $-214 \text{ mV(SCE)}$ . Going to more positive potentials, there are passive current densities higher than those observed in more dilute chloride solutions.

Figure 2a shows the electrochemical behaviour of 316L stainless steel in 3M  $H_3PO_4$  media. The curves in the absence and presence of 0.01 and 0.1M NaCl are similar, showing the passivation of the material and  $E_{\text{trans}} \approx 1020 \text{ mV(SCE)}$ . For 1M NaCl, however, the metal

Table 2 Values of  $E_{\text{corr}}$  for 254SMO stainless steel, 316L stainless steel, and Hastelloy C276 after 16 h immersion in  $H_3PO_4$  solutions in absence and presence of chlorides, mV(SCE)

Solution	254SMO	316L	Hastelloy C276
3M $H_3PO_4$	$181 \pm 60$ (4)*	$209 \pm 9$ (3)	$222 \pm 5$ (4)
3M $H_3PO_4$ + 0.01M NaCl	$268 \pm 27$ (4)	$242 \pm 14$ (4)	$234 \pm 14$ (3)
3M $H_3PO_4$ + 0.1M NaCl	$217 \pm 70$ (5)	$240 \pm 28$ (6)	$226 \pm 4$ (4)
3M $H_3PO_4$ + 1M NaCl	$309 \pm 20$ (3)	$-318 \pm 7$ (3)	$237 \pm 15$ (3)
6M $H_3PO_4$	$257 \pm 8$ (4)	$261 \pm 7$ (4)	$253 \pm 6$ (3)
6M $H_3PO_4$ + 0.1M NaCl	$326 \pm 16$ (2)	$-254 \pm 22$ (3)	$288 \pm 3$ (2)
6M $H_3PO_4$ + 1M NaCl	$-284 \pm 9$ (2)	$-315 \pm 0$ (2)	$327 \pm 8$ (2)

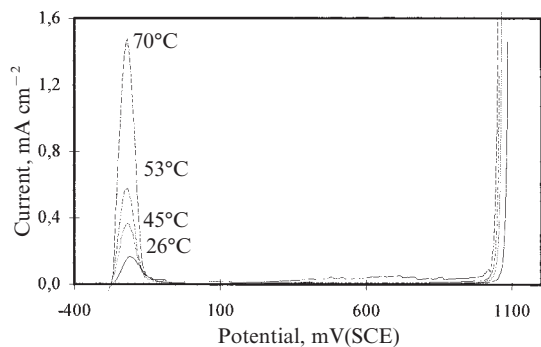
\* Number of experiments carried out.



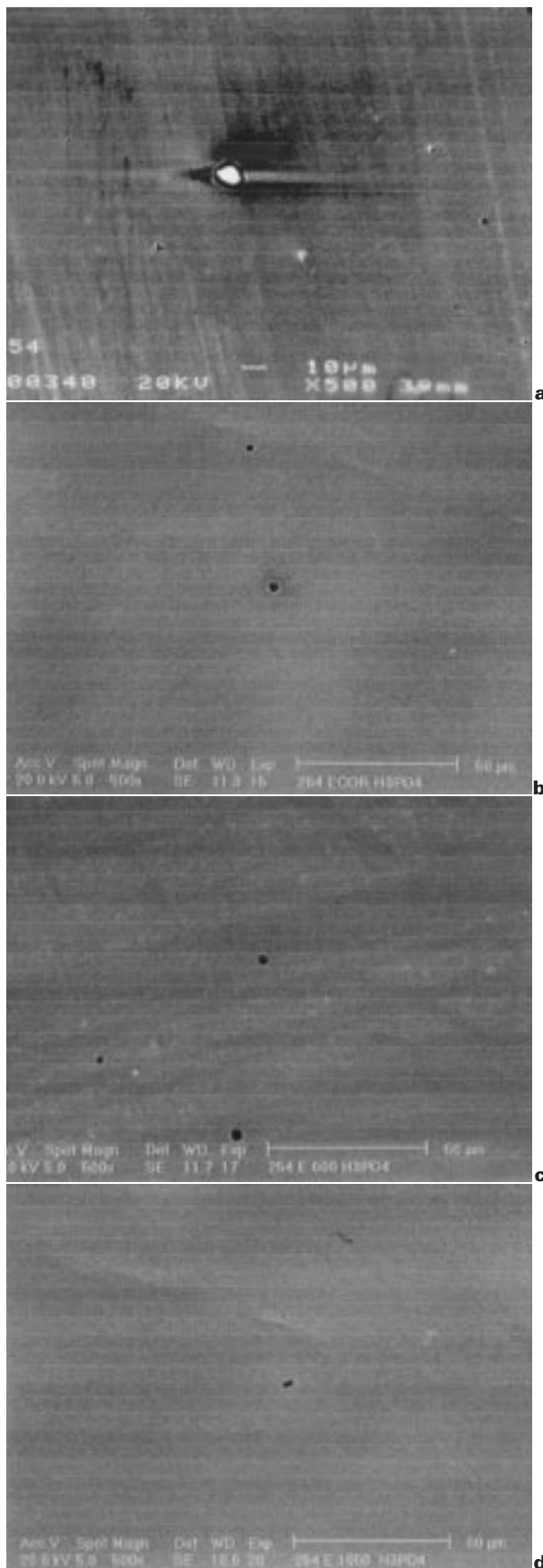
3 Potentiodynamic polarisation curves for Hastelloy C276 in given  $H_3PO_4$  solutions at  $26^\circ C$ : scan rate  $0.5\text{ mV s}^{-1}$

exhibits an active region with  $i_{crit} = 0.45\text{ mA cm}^{-2}$ . The potential at which the current value increases suddenly ( $150\text{ mV(SCE)}$ ) is smaller and the passive current is higher than those observed in other chloride concentrations, suggesting the occurrence of pitting corrosion.

Figure 2b compares 316L stainless steel in 3M and 6M  $H_3PO_4$  solutions, indicating that the  $E_{trans}$  values increase as  $H_3PO_4$  concentrations increase. The same behaviour is observed for 254SMO stainless steel. In 6M  $H_3PO_4$  solutions, 316L stainless steel (Fig.2c) displays three different types of behaviour: in the absence of chloride it is passivated with  $E_{trans} \approx 1050\text{ mV(SCE)}$ , in the presence



4 Effect of temperature on potentiodynamic polarisation curves for 254SMO stainless steel in  $6M\ H_3PO_4 + 1M\ NaCl$  solution: scan rate  $0.5\text{ mV s}^{-1}$



a polished to  $1\ \mu\text{m}$  diamond paste finish; b at open circuit potential; c at  $600\text{ mV(SCE)}$ ; d at  $1050\text{ mV(SCE)}$

5 Scanning electron micrographs of 254SMO, as polished and after exposure for 15 min in  $6M\ H_3PO_4 + 1M\ NaCl$  solution at given potentials

of 0.1M NaCl it exhibits an active region with  $i_{crit} = 0.26 \text{ mA cm}^{-2}$  followed by a passive region up to  $E_{trans} = 1060 \text{ mV(SCE)}$ , and for 1M NaCl it shows an active region with high current densities at  $-310 \text{ mV(SCE)}$ .

Hastelloy C276 exhibited passive behaviour in all the media studied. This behaviour is confirmed by the positive  $E_{corr}$  values referred to previously and by the potentiodynamic polarisation curves presented in Fig. 3.

Figure 4 shows the effect of temperature on the anodic polarisation curves for 254SMO stainless steel in a 6M  $\text{H}_3\text{PO}_4$  solution containing 1M NaCl. It can be seen that  $i_{crit}$  values increase as temperature increases, but the material is passivated and has  $E_{trans} \approx 1040 \text{ mV(SCE)}$  at temperatures ranging from 25 to  $70^\circ\text{C}$ , indicating the absence of pitting.

Figure 5a shows the surface of the 254SMO steel as observed by SEM after polishing to a  $1 \mu\text{m}$  finish with diamond paste. A few inclusions can be seen. Figure 5b-d shows the appearance of the 254SMO steel following exposure to 6M  $\text{H}_3\text{PO}_4 + 1\text{M NaCl}$  solution for 15 min at the open circuit potential, at 600 mV(SCE), and at 1050 mV(SCE). The surface appearance in these three cases is similar to that shown in Fig. 5a, showing the absence of any significant corrosion process and the presence of a few inclusions.

## CONCLUSIONS

This work permits the following conclusions to be made:

1. Stainless steel 254SMO has better corrosion resistance than 316L stainless steel and almost the same corrosion resistance as Hastelloy C276 in phosphoric acid media in the absence and presence of chloride ions.

2. The 254SMO is passivated in 3M  $\text{H}_3\text{PO}_4$  solutions containing  $[\text{Cl}^-] \leq 1\text{M}$ .

3. The 254SMO is passivated in 6M  $\text{H}_3\text{PO}_4$  solutions containing  $[\text{Cl}^-] \leq 0.1\text{M}$ .

4. The 254SMO is active in 6M  $\text{H}_3\text{PO}_4$  solutions containing 1M NaCl, with critical current densities varying from  $0.16 \text{ mA cm}^{-2}$  at  $25^\circ\text{C}$  to  $1.47 \text{ mA cm}^{-2}$  at  $70^\circ\text{C}$ .

## ACKNOWLEDGEMENTS

The authors are grateful to FAPESP (Foundation for the Support of São Paulo State Research) and CNPq (Brazilian Scientific and Technological Development Council) for research grants.

## REFERENCES

1. A. GUENBOUR, J. FAUCHEU, and A. B. BACHIR: *Corrosion*, 1988, **44**, (4), 214.
2. B. LINDER: *Ind. Corros.*, 1987, **5**, (3), 12-17.
3. L. DE MICHELI: 'Estudo comparativo da resistência à corrosão por pite dos aços inoxidáveis austeníticos 254, 316 e 304 em meios de cloreto', master's thesis, Institute of Chemistry of USP, São Paulo, Brazil, May 1994.
4. L. DE MICHELI and S. M. L. AGOSTINHO: Proc. 34th Brazilian Conf. on Chemistry, Porto Alegre, Brazil, October 1994.
5. L. DE MICHELI, C. A. BARBOSA, and S. M. L. AGOSTINHO: Proc. 18th Annual Meeting of Brazilian Society of Chemistry, Caxambu, MG, Brazil, May 1995.
6. R. QVARFORT: *Corros. Sci.*, 1989, **29**, (8), 987.
7. J. OLSSON: *Stainless Steel Ind.*, Jan. 1990, **18**, (101).
8. J. OLSSON and H. GRUTZNER: *Werkst. Korros.*, 1989, **40**, (5), 279.
9. N. ALONSO: 'Análise do método potenciodinâmico de determinação do potencial de pite', doctoral thesis, Escola Politécnica da USP, São Paulo, Brazil, 1992.

# Concepts in the Electron Theory of Alloys

Alan Cottrell

**B705 ISBN 1 86125 075 4 Hbk 136pp**

**European Union £20/Members £16**

**Non-European Union \$40/Members \$32**

**p&p European Union £5.00/Non-EU \$10.00 per order**

Orders to: IOM Communications Ltd, Shelton House, Stoke Road, Shelton,  
Stoke-on-Trent ST4 2DR Tel: +44 (0) 1782 202 116 Fax: +44 (0) 1782 202 421  
Email: [Orders@materials.org.uk](mailto:Orders@materials.org.uk) Internet: [www.materials.org.uk](http://www.materials.org.uk)



IOM Communications

Reg. Charity No. 1059475 VAT Registration No. GB 649 1646 11

IOM Communications Ltd is a wholly owned subsidiary of the Institute of Materials