Electrochemical behaviour of 254SMO stainless steel in comparison with 316L stainless steel and Hastelloy C276 in HCl media

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

The electrochemical behaviour of 254SMO stainless steel in HCl solutions has been studied and compared with that observed for other alloys using open circuit potential measurements, potentiodynamic polarisation curves, and SEM analysis techniques. 254SMO does not display pitting corrosion at room temperature in HCl solutions having concentrations ⩽5·0M. Its performance is comparable with that of Hastelloy C276 in HCl media in solutions of strength ⩽1·0M. The critical pitting temperature for 254SMO exceeds 76°C in 3M HCl solutions.

Dr De Micheli and Dr Agostinho are in the Institute of Chemistry of University of São Paulo (IQUSP), Av. Prof. Lineu Prestes, 748-B3i São Paulo, SP, Brazil. Dr Barbosa is with Villares Metals SA, Sumaré, SP, Brazil. Dr Andrade is in the Institute of Research Energetic and Nuclear (IPEN), São Paulo, Brazil. *Manuscript received 2 July 1999; accepted 15 November 1999.*

INTRODUCTION

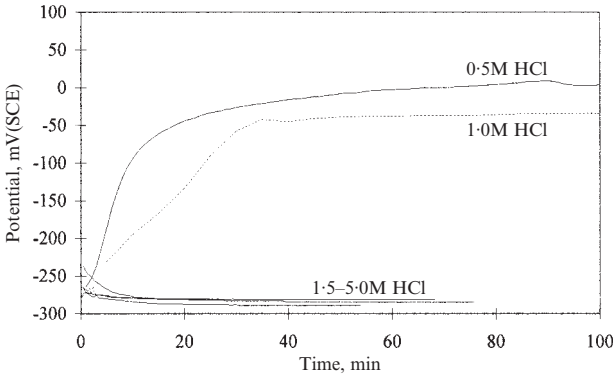
Stainless steel to the 254SMO designation (UNS S31254) contains higher quantities of chromium, nickel, molybdenum, and nitrogen than common stainless steels such as types 304, 316, and 316L. The synergistic effect of these alloying elements promotes improved corrosion resistance in chloride media.[1,2] The steel was developed 20 years ago, but there have been relatively few studies on its performance.[3–11] Olson[10,11] showed 254SMO steel to be a material with excellent resistance to corrosion in halide solutions. Qvarfort[5] determined its critical pitting temperature to be about 89°C in 5M NaCl aqueous solutions. The corrosion resistance of 254SMO in acid chloride media has not been reported in the literature.

The aim of the present work was to study the electrochemical behaviour of 254SMO in HCl solutions and to compare its corrosion resistance with that observed for other metallic materials.[12,13] Techniques used in the study included open circuit potential measurements, potentiodynamic polarisation curves, and microstructural analyses.

EXPERIMENTAL

Table 1 presents the chemical compositions of the alloys studied and their respective electrode areas. The 254SMO (UNS S31254) was compared with 316L (UNS S31603), Hastelloy C276 (UNS S10276), and titanium (UNS R56400).

Disc electrodes mounted in polytetrafluoroethylene (PTFE) were used as working electrodes and electrical contact was made via a brass rod. The electrode was mounted in a cylinder of PTFE of a slightly smaller diameter than the metallic material, and hot mounting was used to avoid crevice corrosion. A saturated calomel electrode (SCE) was used as the reference electrode. A large piece of platinum foil was used as the auxiliary electrode.



1 *Open circuit potential transient for 254SMO in HCl solutions at 25°C*

The electrodes were ground using 320, 400, and 600 grit abrasive papers and were then rinsed in water followed by ethanol before being air dried.

A PAR 273A potentiostat and a Philips XL-30 scanning electron microscope were used to obtain polarisation curves and microstructural information respectively.

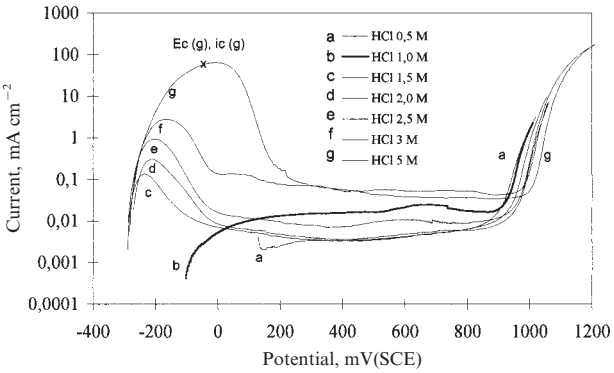
The solutions were prepared from analytical grade reagents and doubly distilled water.

RESULTS AND DISCUSSION

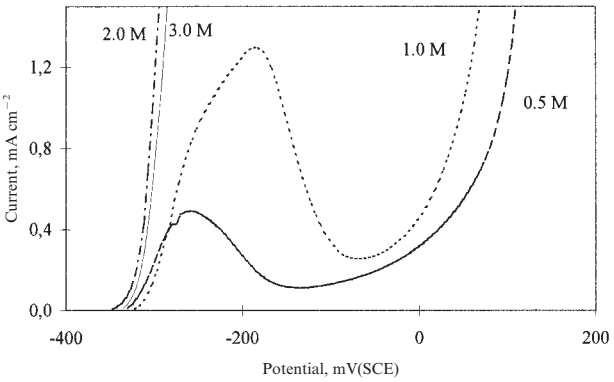
Figure 1 presents the open circuit potential transients for 254SMO steel in HCl solutions of various concentrations. It can be seen that the stationary potential value (considered

Table 1 Specific chemical composition of studied metallic materials (wt-%) and electrode areas S_e

	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	N	Ti	V	Others	Fe	S_e, cm^2
254SMO	0·02	0·42	0·49	0·02	0·004	20·1	6·42	18·4	0·77	0·21	…	…	…	Bal.	1·02
316L	0·02	0·50	1·71	0·03	0·023	16·2	2·18	11·0	0·35	0·07	…	…	…	Bal.	0·48
Hastelloy C276	0·01	0·09	0·28	0·01	0·015	16·0	15·5	Bal.	0·01	…	…	0·25	W 3·67	6·32	0·48
Titanium	0·02	0·09	0·03	…	0·002	0·27	0·07	…	…	…	Bal.	3·84	Al 6·71	0·36	0·28



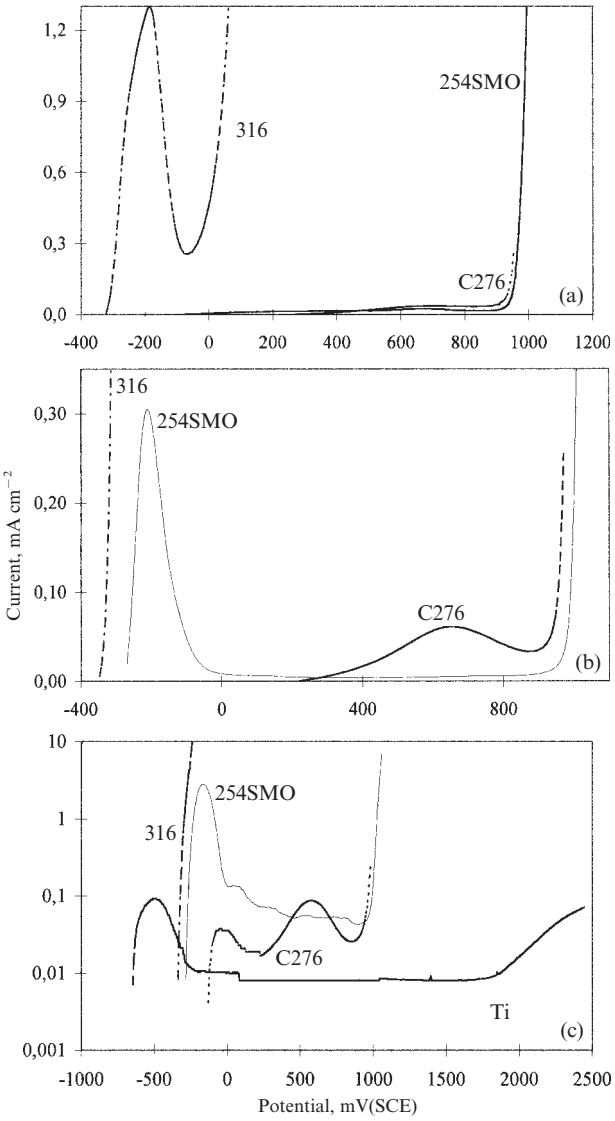
2 *Potentiodynamic polarisation curves for 254SMO in HCl solutions at 25°C*



3 *Potentiodynamic polarisation curves for 316L in HCl solutions at 25°C*

in this work to be the corrosion potential E_{cor}) was attained within 40 min. Two types of behaviour can be observed in the variation of open circuit potential as a function of time. For [HCl] < 1·5M the potential values increased with increasing time, suggesting the presence of a passive layer, whereas for [HCl] ⩾ 1·5M the potential values decreased as time increased, suggesting that the metal was active in these media. It was also observed that there was a considerable variation in the E_{cor} values for [HCl] = 1M (Table 2), suggesting that this concentration is very close to that for the transition between passive and active behaviour for the steel. Figure 2 presents anodic potentiodynamic curves and Table 2 shows the critical current density i_c, passivating current density i_p, and critical potential E_c values for 254SMO in HCl media. A large passive region and transpassivation potential values higher than 900 mV (SCE) were observed. For [HCl] ⩽ 1·0M the material is not active in these media, but when [HCl] ⩾ 1·5M there is an active region, confirming what was expected from the E_{cor} values.

It can be seen that i_p values are about 5×10^{-3} mA cm^{-2} for [HCl] ⩽ 2·5M, but they become 10 times higher for



a 1M; *b* 2M; *c* 3M

4 *Potentiodynamic polarisation curves for 254SMO, 316L, Hastelloy C276, and titanium in HCl at 25°C*

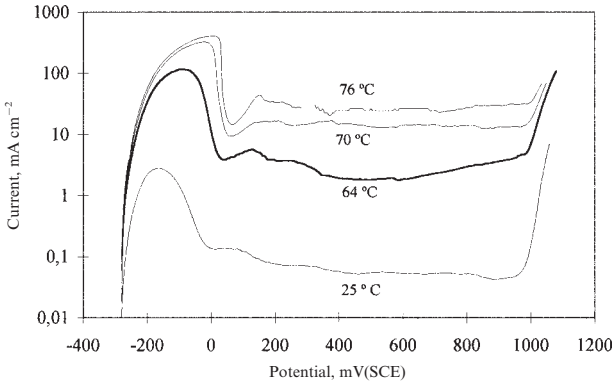
[HCl] > 2·5M. For [HCl] ⩾ 1·5M the E_{cor} values do not depend on the HCl concentration and the i_c values increase as the HCl concentration increases owing to the greater aggressiveness of the solution, hindering passivation and generating more positive critical potentials E_c. The data in Table 2 also show that transpassivation potential values increase as [HCl] increases, owing to the thermodynamic dependence of the water oxidation potential on pH.[1]

A different behaviour in HCl media is observed for 316L, as can be seen from Fig. 3. The active region occurs at [HCl] ⩾ 0·5M and the passivating film is destroyed at

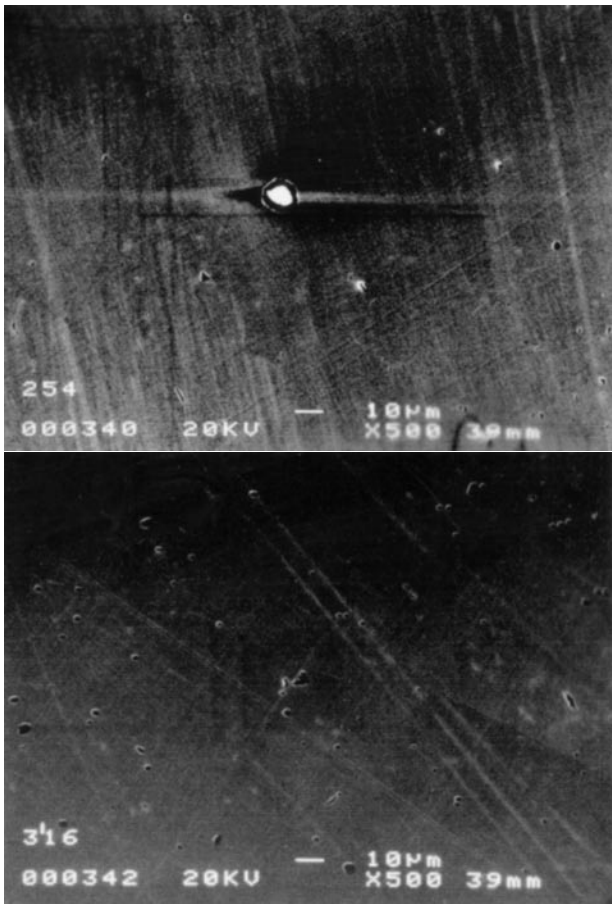
Table 2 Polarisation curve parameters* for 254SMO in HCl media at 25°C

[HCl], M	E_{cor}, mV(SCE)	i_p, mA cm^{-2}	i_c, mA cm^{-2}	E_c, mV(SCE)
0·5	33 ± 16	0·003	…	…
1·0	57 ± 148	0·005 ± 0·005	…	…
1·5	−284·5 ± 0·5	0·005 ± 0·001	0·142 ± 0·007	−234 ± 1(2)
2·0	−282·6 ± 6·7	0·005 ± 0·001	0·31 ± 0·04	−222 ± 6
2·5	−283·5 ± 3·5	0·004 ± 0·004	0·8 ± 0·1	−199·5 ± 3·5
3·0	−282·7 ± 2·4	0·04 ± 0·02	2·6 ± 0·3	−168 ± 2
5·0	−285 ± 4	0·07 ± 0·04	70 ± 5·5	−2·5 ± 2·5

* E_{cor} corrosion potential, i_p passivating current density, i_c critical current density, E_c critical potential.



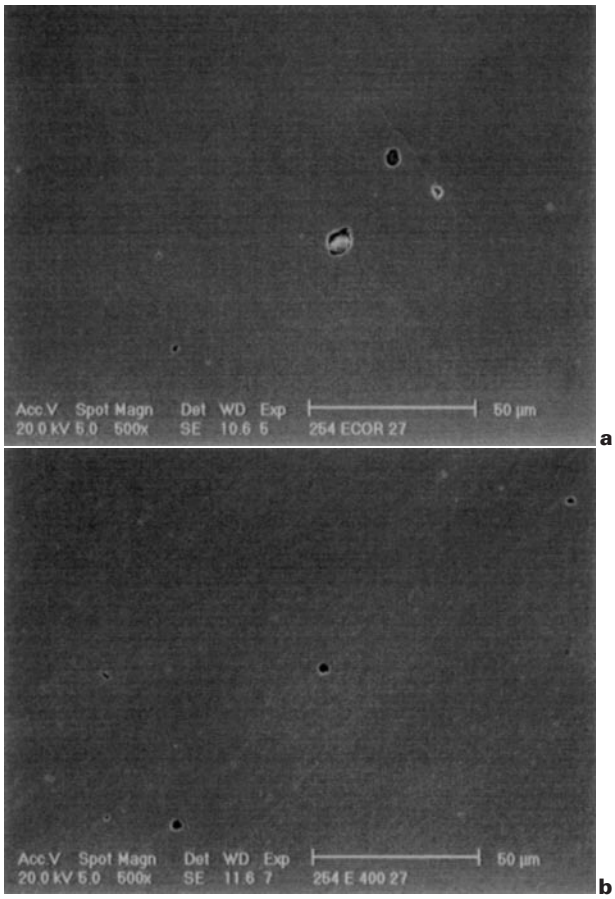
5 *Anodic potentiodynamic polarisation curves for 254SMO in 3M HCl at different temperatures*



6 *Scanning electron micrographs of 254SMO (top) and 316L (below) after polishing with 1 μm diamond paste*

lower potential values than is the case for 254SMO. It can also be observed that i_c values increase and the passive region is shortened as [HCl] increases and the material is not passivated for [HCl] $\geqslant$ 2M. This active behaviour is confirmed by the negative E_{cor} values of $-425{\cdot}5 \pm 0{\cdot}5$, -415 ± 3, and $-399{\cdot}5 \pm 0{\cdot}5$ mV(SCE) for 316L in 0·5, 1·0, and 3·0M HCl respectively.

Figure 4 presents comparisons between 254SMO and the other alloys studied in HCl solutions. 254SMO behaves similarly to Hastelloy C276 in 1M HCl and is passivated over the entire range of potentials studied until the oxygen evolution reaction potential is attained ($\sim$1000 mV(SCE)), while 316L displays increasing current at low potential values of about 0 mV(SCE), suggesting the occurrence of pitting. In 2M HCl the 254SMO steel is more active than Hastelloy C276, but the high transpassivation potential



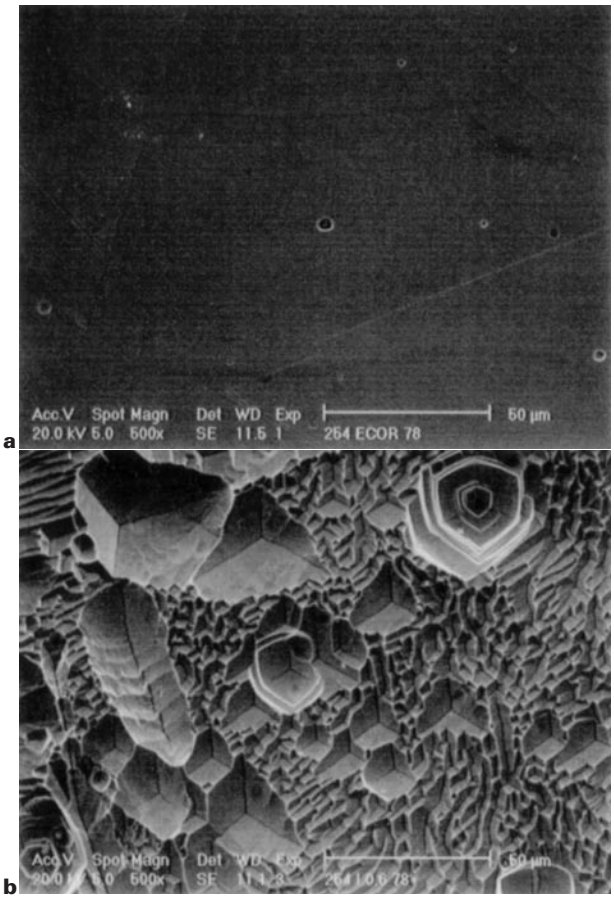
a after 30 min at open circuit potential (−283 mV(SCE)); *b* after 15 min at 400 mV(SCE)

7 *Scanning electron micrographs of 254SMO in 3M HCl at 27°C*

values and the absence of hysteresis suggest the absence of pitting of 254SMO in this medium. In 3M HCl (Fig. 4*c*) the 254SMO steel, although active at lower potential, displays passive current density values comparable with those for Hastelloy C276, neither does it show pitting corrosion, for the reasons explained above. Titanium is active at more negative potentials, with the lowest E_{cor} value, but it displays a large passive region from −250 to +1800 mV(SCE), indicating a high oxygen evolution overpotential in this medium.

The different behaviour displayed by the materials in HCl solutions reflects their chemical composition. The presence of larger contents of chromium, nickel, molybdenum, and nitrogen in the 254SMO stainless steel compared with 316L stainless steel promotes the corrosion resistance of the former alloy. The 254SMO stainless steel has corrosion resistance comparable with that observed for Hastelloy C276 in most of the environments, at much lower cost. Titanium is the most resistant material in HCl media but is much more expensive. Hastelloy C276 displayed a current peak at potentials of around 650 mV(SCE) that increased with increasing HCl concentration; this peak is probably due to the dissolution of molybdenum.[13]

Figure 5 presents anodic potentiodynamic polarisation curves for 254SMO in 3·0M HCl at different temperatures. It can be seen that i_c and i_p values become higher as the temperature increases, but the transpassivation potential was not changed and no hysteresis was observed, suggesting that the critical pitting temperature had not yet been attained. In this range of temperatures (64–76°C), corrosion occurs over the entire range of potentials, as shown by the higher current values, in spite of the fact that the surface is partially passivated.



a after 30 min at open circuit potential; *b* after 15 min at −250 mV(SCE)

8 *Scanning electron micrographs of 254SMO in 3M HCl at 76°C*

a after 30 min at open circuit potential; *b* after 15 min at −250 mV(SCE)

9 *Scanning electron micrographs of 316L in 3M HCl at 27°C*

Figure 6 presents SEM observations of 254SMO and 316L steels after polishing with 1 µm diamond paste.

Figure 7*a* shows a scanning electron micrograph of 254SMO after 30 min at the open circuit potential (−283 mV(SCE)) in 3M HCl at 27°C. A clean surface with a few inclusions can be seen, similar to that shown in Fig. 6*a* for the polished surface. The same is true after 15 min at 400 mV(SCE), as shown in Fig. 7*b*. No evidence of pitting is observed in either case. At 76°C the surface did not change after 30 min at the open circuit potential (Fig. 8*a*), and this behaviour is identical to that observed in Figs. 6*a* and 7*a* and *b*. However, when the potential is changed to −250 mV(SCE), strong general attack occurs at 76°C, as shown in Fig. 8*b*, after only 15 min at this potential ($i = 0{\cdot}2$ A cm^{-2}).

The presence of pitting can be seen on 316L in 3M HCl at 27°C, after 30 min at the open circuit potential, as shown in Fig. 9*a*. After 15 min at −250 mV(SCE) the number and size of pits increases and they are formed at the grain boundaries and at sites within the grain (Fig. 9*b*).

CONCLUSIONS

1. Electrochemical measurements suggest that 254SMO does not undergo pitting corrosion at room temperature in HCl media when $0{\cdot}1\text{M} \leqslant [\text{HCl}] \leqslant 3\text{M}$.

2. Potentiodynamic polarisation curves show that 254SMO has comparable performance to Hastelloy C276 in HCl media when $[\text{HCl}] \leqslant 1{\cdot}0\text{M}$, with passive film formation over the entire range from the corrosion potential to the transpassivation potential at room temperature.

3. 254SMO displays a critical pitting temperature in excess of 76°C in 3M HCl, based on potentiodynamic measurements.

4. 316L undergoes pitting corrosion in 3M HCl at 27°C.

ACKNOWLEDGEMENTS

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

REFERENCES

1. R. C. NEWMAN and T. SHAHRABI: *Corros. Sci.*, 1987, **27**, (8), 827.
2. J. KOLTZ, J. B. C. WU, P. E. MANNING, and A. I. ASPHAHANI: *Corros. Rev.*, 1986, **6**, (4), 279.
3. L. DE MICHELI, A. H. P. ANDRADE, C. A. BARBOSA, and S. M. L. AGOSTINHO: *Br. Corros. J.*, 1999, **34**, (1), 67–70.
4. L. DE MICHELI, A. H. P. ANDRADE, C. A. BARBOSA, M. TESSLER, and S. M. L. AGOSTINHO: 'Electrochemical behaviour of UNS S31254 Brazilian made steel in chloride media', Master's thesis, Instituto de Química da USP, São Paulo, Brazil, 1994.
5. R. QVARFORT: *Corros. Sci.*, 1989, **29**, (8), 987.
6. L. DE MICHELI, C. A. BARBOSA, and S. M. L. AGOSTINHO: Proc. 18th Annual Meeting of Brazilian Society of Chemistry, Caxambu, MG, Brazil, 1995.
7. L. DE MICHELI and S. M. L. AGOSTINHO: Proc. 34th Brazilian Congress on 'Chemistry', Porto Alegre, RS, Brazil, October 1994.
8. A. GARNER: *Pulp Paper Can.*, 1981, **82**, (12), 109.
9. A. GARNER: Proc. 25th Annual Conference of Metallurgists: 'High performance austenitic stainless steels in the pulp and paper industry', August 1986, CIM.
10. J. OLSSON: *Stainless Steel Ind.*, 18 January 1990, 101.
11. J. OLSSON and H. GRUTZNER: *Werkst. Korros.*, 1989, **40**, (5), 279.
12. M. HARA and Y. SHINATA: *Corros. Sci.*, 1990, **31**, 691.
13. P. McKAY and D. B. MITTON: *Corrosion*, 1985, **41**, (1), 52.