Metallurgy and materials
Metalurgia e materiais

Effect of sulfate on the pitting potential of austenitic stainless steels 18Cr8Ni and 17Cr6Mn5Ni in chloride media

José Wilmar Calderón-Hernández[1,3]

http://orcid.org/0000-0003-2280-6761

Duberney Hincapíe-Ladino[1,4]
Rodrigo Magnabosco[2,5]
Neusa Alonso-Falleiros[1,6]

[1]Universidade de São Paulo- USP, Escola Politécnica, Departamento de Engenharia Metalúrgica e de Materiais, São Paulo – São Paulo – Brasil.

[2]FEI University, Departamento de Engenharia de Materiais, São Bernardo do Campo – São Paulo – Brasil.

E-mails: [3]wilmarcalderon100@gmail.com, [4]duberneyhincapie@gmail.com, [5]rodrmagn@fei.edu.br , [6]nealonso@usp.br

Abstract

Pitting corrosion resistance of two austenitic stainless steels, 18Cr8Ni (Type 304L or UNS S30403 stainless steel) and 17Cr6Mn5Ni, was evaluated in three electrolytic solutions containing a fixed concentration of 0.6M sodium chloride and different additions of sodium sulfate, 0.06M, 0.15M or 0.6M. Cyclic potentiodynamic polarization tests were performed on as-received samples and on specimens annealed at 1010°C, 1040°C, 1070°C or 1100°C. The best pitting corrosion resistance was presented by the 17Cr6Mn5Ni steel annealed at 1070°C or 1100°C, with lower delta ferrite contents, in the electrolyte with the highest sulfate concentration. It can be found that the addition of sodium sulfate inhibits pitting corrosion and has a better inhibitor effect in the high manganese steel.

Keywords: pitting potential; sodium chloride; stainless steel; manganese; corrosion inhibitor.

1. Introduction

The historical problem of nickel price oscillations has propelled investigations on the use of other austenitizing elements in austenitic stainless steels, especially manganese (Charles, 2005). Some investigations on the corrosion behavior of Mn alloyed austenitic stainless steel reported that Mn promoted a negative effect on the corrosion resistance (Condylist *et al.*, 1970; El Dim *et al.*, 1972; Lunarska *et al.*, 1975; Murgulesco and Radovici, 1990 and Knyazheva *et al.*, 1965). How-

ever, these researches were executed using electrolytic solutions based on sulfuric acid (H_2SO_4), which is not appropriate for studying pitting corrosion. Acid solutions are frequently used to test uniform corrosion and the passive film performance.

Kemp (1995) studied the effect of Mn on general and pitting corrosion of Cr-Mn duplex stainless steels (with 3 to 10%wt Mn), using cyclic polarization electrochemical tests in 0.025N NaCl, and anodic polarization in 0.1N H_2SO_4,

revealing that Mn addition reduced both general and pitting corrosion resistance. The latter was thought to be caused by a possible increase in the amount of Mn inclusions (sulfide and oxide types) with an increase of the Mn content. As a matter of fact, the pit nucleation in stainless steels is usually associated with the presence of MnS inclusions (Pardo *et al.*, 2008; Ryan *et al.*, 2002 and Schmuki *et al.*, 2005). In the steels used in the present investigation, there is not expected a considerable

occurrence of MnS due to low S content (10 and 20 ppm) obtained in today's steel making practice.

On the other hand, the presence of delta ferrite (δ-ferrite) in austenitic stainless steels is also known as a concern when pitting corrosion resistance is required. Literature presents several investigations about the effect of δ-ferrite on the pitting corrosion resistance of austenitic stainless steel and the results are divergent. Some investigations have shown that δ-ferrite had a detrimental effect on pitting corrosion resistance, the general explanations are that its formation causes Cr depletion in the surrounding γ-matrix and increased the amount of δ/γ interfaces, and consequently increasing the number of preferential pit nucleation sites (Sedriks, 1996; Szklarska, 1986 and Manning and Duquette, 1980). Other articles report that the presence of delta ferrite was not detrimental to corrosion resistance. Lunarska *et al.* (1975), when studying Cr-Ni-Mn steel found that the δ-ferrite was not attacked in chloride media. In the article of Nair and Semchiysen (1963), Cr-Ni-Mn (containing Mo) steel, under weakly oxidizing acidic conditions, was not affected by the δ-ferrite presence. Chatoraj *et al.*, (1996) argue that delta

ferrite is not detrimental to pitting corrosion resistance, but the products from delta ferrite, i.e., its formation in the sigma phase, was found to be responsible for the deterioration of corrosion resistance. Recently Calderón-Hernández *et al.*, (2015) showed that a proper annealing treatment in austenitic stainless steels 18Cr-8Ni and 17Cr6Mn5Ni (the same steels and treatments used in the present investigation) can reduce or eliminate δ-ferrite of the microstructure. It was also shown that the pitting potential in 0.6M NaCl was not affected by δ-ferrite content. In these investigations, possibly the electrolytes were very aggressive and did not reveal the differences in corrosion resistance associated to the presence of δ-ferrite.

Galvele (1974) reported that through analysis of the transport processes inside the pit, the pitting potential of a metal should change with Cl- ion concentration according to the equation: Ep = Ep° - B*log[Cl⁻]; with B = 0.059V being the slope of the curve at room temperature. Nevertheless, the chemical composition of the bulk material is not directly taken into account, and the contribution is applied for the study of pit growing, not pit initiation, which is the focus of the present investigation. The literature on the inhibi-

tion effect produced by the sulfate ion on pitting corrosion of stainless steels is scarce, especially in the case of new stainless steels which contain low C and low S, and controlled quantity of precipitates and non-metallic inclusions (Colpaert, 2008). One of the first contributions on this subject is credited to Leckie and Uhlig, (1966), who performed potentiodynamic polarization tests with18Cr-8Ni stainless steel in various electrolytes containing Na_2SO_4 and a fixed content of 0.1M NaCl, reporting the inhibition effect of sulfate ion over pitting corrosion.

This investigation presents the influence of sulfate ion concentration (when added to electrolytes containing chloride ions) and the influence of the annealing temperature and consequently the influence of different delta ferrite contents, on pitting corrosion resistance of two austenitic stainless steels with different Mn and Ni addictions. The major contribution of this article relies on the investigation of the influence that Mn addition in a stainless steel can have on the pitting corrosion inhibitor characteristic of the sulfate addition in chloride media, especially in the pit nucleation stage, analyzed through pitting potential measurements.

2. Materials and experimental procedures

The material was received as 2.8 mm thickness hot-rolled plates of 17Cr6Mn-5Ni steel, and 4 mm thickness hot-rolled plates of UNS S30403 steel (Type 18Cr8Ni steel). Square samples of 10mm sides were cut and then annealed at 1010°C, 1040°C, 1070°C or 1100°C for 20 minutes and quenched in water. The chemical composition of the steels is shown in Table 1.

Steel	C	**Mn**	Cr	**Ni**	P	Si	S	Mo	N	Cu	Co
17Cr6Mn5Ni	0.029	**5.82**	17.2	**4.64**	0.035	0.32	0.001	0.023	0.0615	1.56	0.047
18Cr8Ni	0.017	**1.54**	18.5	**8.03**	0.035	0.44	0.002	0.047	0.0483	0.05	0.1

Table 1
Chemical composition of 18Cr8Ni and 17Cr6Mn5Ni steels.

Cyclic Potentiodynamic Polarization tests (CPP) were conducted using three electrolytes with a fixed concentration of 0.6M NaCl and with different Na_2SO_4 additions (0.06M, 0.15M or 0.6M) for the determination of the pitting potential (Ep). At least ten CPP curves were acquired for each condition to calculate the average and standard deviation of Ep. CPP tests were executed using a saturated calomel

electrode as reference electrode (SCE), and a platinum wire (1mm diameter, 20 cm long, in a spiral form) as counter electrode. To run the tests, samples were previously immersed during 5 minutes to start the polarization in anodic direction beginning from open circuit potential (OCP), with a scan rate of 1mV/s, and when a current density of 10^{-3} A/cm² was reached, the polarization is reverted until the curve

completes the loop (Figure 4).

Microstructural characterization was performed over polished samples after electrolytic etching in 10% oxalic acid aqueous solution using Optical Microscopy, X-Ray Diffraction (XRD) under Cu-Kα1 radiation, and measurement of ferrite volume fraction by quantitative stereology of digitally treated images, aided the microstructural characterization.

3. Results

Figure 1 presents typical microstructures of the steels in the N/A condition and after the annealing treatments. In the N/A conditions, islands

of a phase different from the austenite matrix can be observed (Figures 1a and 1b). In the materials annealed at 1010 °C, this phase decreases par-

tially (Figures 1c and 1d) and in the materials annealed at 1100 °C these islands almost completely disappear (Figures 1e and 1f).

17Cr6Mn5Ni N/A

18Cr8Ni N/A
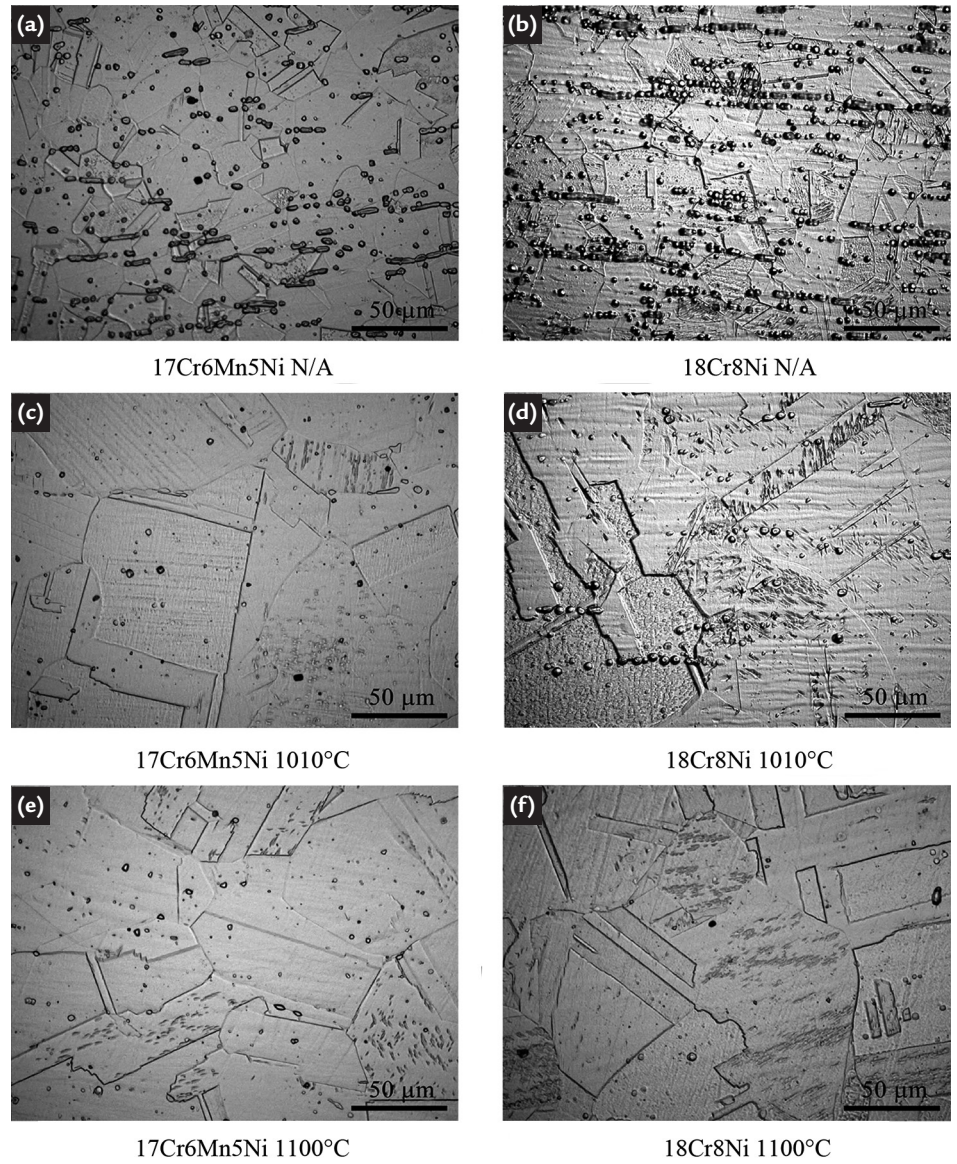
17Cr6Mn5Ni 1010°C

18Cr8Ni 1010°C

Figure 1
Typical microstructures of:
a) 17Cr6Mn5Ni not-annealed; b) 18Cr8Ni
not-annealed; c) 17Cr6Mn5Ni annealed
at 1010°C; d) 18Cr8Ni annealed at 1010°C;
d) 17Cr6Mn5Ni annealed at 1100°C and
f) 18Cr8Ni annealed at 1100°C. MO after
electrolytic etching in 10% oxalic acid.

17Cr6Mn5Ni 1100°C

18Cr8Ni 1100°C

X-ray diffraction patterns analysis (Figure 2) identified that both steels were composed of austenite (γ) and δ-ferrite phases. Chemical composition analysis by EDS determined that the islands of the other phase were chromium-rich, confirming that they are δ ferrite islands.

Figure 2
XRD patterns of the steels
in the not-annealed (N/A)
condition and annealed at 1100°C.
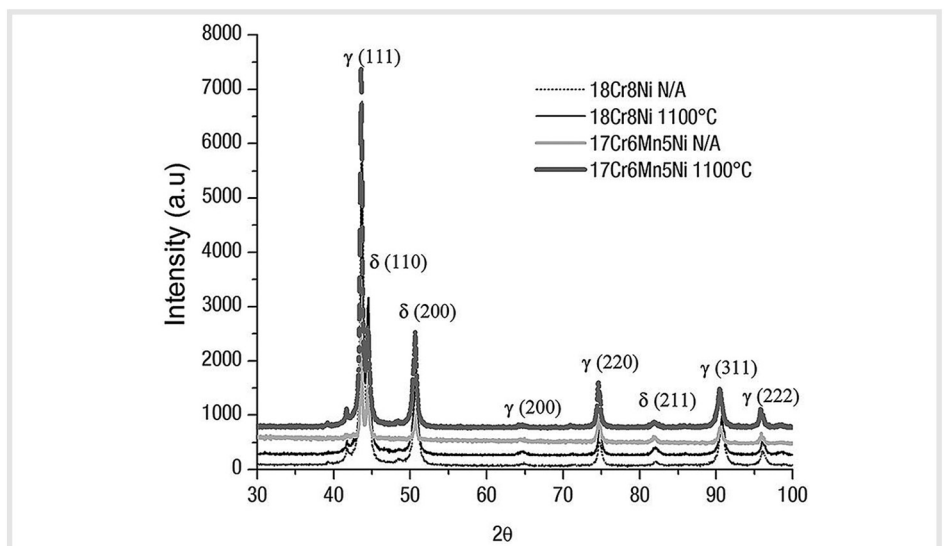
The ferrite volume fraction was measured by quantitative stereology (Figure 3); the ferrite volume fractions in the N/A condition were around 4.5% for the 18Cr8Ni steel and 2.2% for the 17CR6Mn5Ni steel. Increas-

ing annealing temperature leads to a reduction in the ferrite volume. It is worth noting that an increase in the annealing temperature in the temperature range studied, promoted only a small reduction in the ferrite content (for the 17Cr6Mn5Ni, 1% after 1010°C annealing to 0.8% after 1100°C annealing).
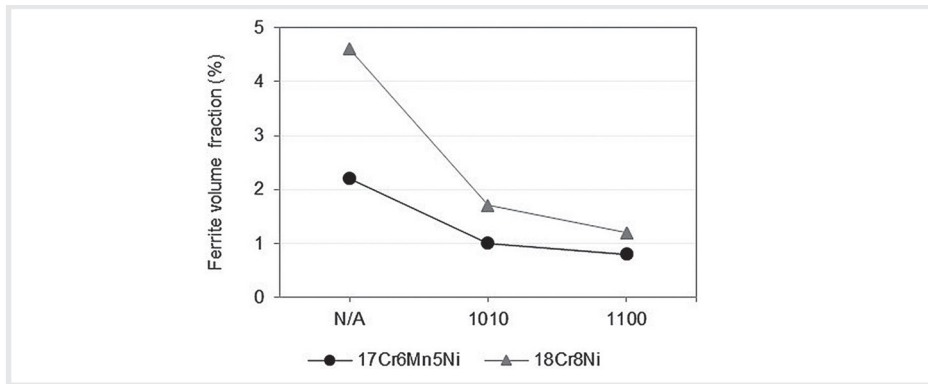

Figure 3
Ferrite volume fraction of the 18Cr8Ni and 17Cr6Mn5Ni steels measured by quantitative stereology.

Representative curves obtained in CPP tests for all conditions are shown in Figure 4. The obtained curves presented both a well-defined passive zone and pitting potential. It was observed that all tests presented hysteresis looping.
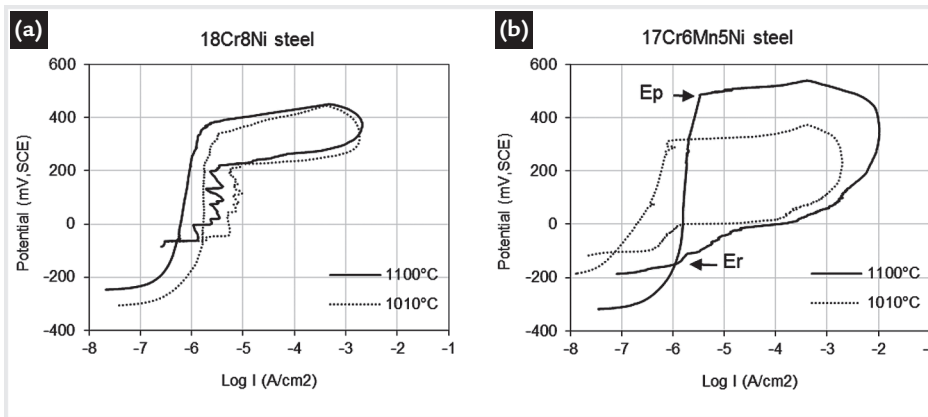

Figure 4
CPP representative curves obtained for 18Cr8Ni and 17Cr6Mn5Ni steels treated at 1010°C and 1100°C. Electrolyte 0.6M Na_2SO_4 + 0.6M NaCl. (Ep: Pitting potential; Er: Repass potential).

Figure 5 shows Ep values as a function of annealing temperature (N/A is the not-annealed condition). In previous investigation (Calderón-Hernández *et al.*, 2015) the results of Ep using blank solution (without Na_2SO_4 addition, only 0.6M NaCl) where obtained, and these results are added to Figure 5 with the purpose of reinforcing the aim of the present investigation.
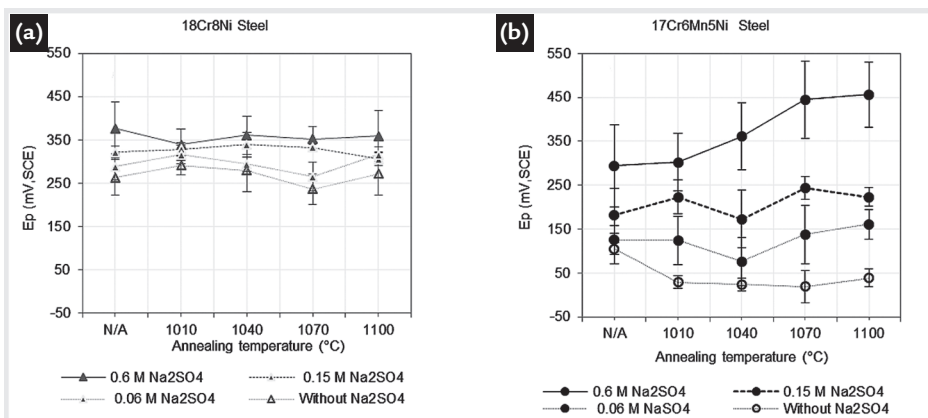

Figure 5
Ep values for (a) 18Cr8Ni and (b) 17Cr6Mn5Ni austenitic steel as a function of annealing temperature for the three containing sulfate electrolytes. The results of blank solution (Without Na_2SO_4, only 0.6M NaCl) were obtained from previous investigation (Calderón-Hernández et al., 2015).

The Ep results obtained for the 18Cr8Ni (Figure 5a) showed a slight dependence with the addition of Na_2SO_4 in the electrolyte, since higher sulfate concentrations lead to slightly higher Ep, although the Ep was practically independent of the annealing temperature, and are higher than Ep values for the 17Cr6Mn5Ni steel. Only in the 0.6M NaCl + 0.6M Na_2SO_4 electrolyte, 17Cr6Mn5Ni steel heat treated at 1070°C and 1100°C was there a higher pitting potential than 18Cr8Ni. However, the Ep results obtained for the 17Cr6Mn5Ni steel (Figure 5b) showed high dependence with the additions of Na_2SO_4 in the electrolyte. In general, the Ep in the electrolytes containing smaller amounts of Na_2SO_4 (0.06M and 0.15M) did not show significant dependence with the annealing temperature, but the tests performed with the most concentrated electrolyte (0.6M Na_2SO_4) exhibited greater dependence with this parameter.

4. Discussion

Figure 5 shows that 18Cr8Ni steel reacted slightly to the inhibitor effect of Na_2SO_4 additions and that the annealing treatment has negligible. It can be also observed in Figure 5 that the Na_2SO_4 additions increase the Ep in both steels and in all heat treatment conditions, demonstrating its inhibitor effect on the pitting corrosion, but this inhibitor effect was stronger in the steel containing high Mn. Moreover, when analyzing the electrolytes separately, in general, it can be observed that the behavior of the Ep as a function of the annealing temperatures only showed relevant dependency for the high Mn steel in the electrolytic solution containing the highest sulfate concentration, 0.6M NaCl + 0.6M Na_2SO_4.

The inhibitor effect of Na_2SO_4 can be discussed by means of the chemical affinity between chloride and sulfate ions in the adsorption stage, which can be evaluated through standard Gibbs free energy of formation of compounds ($\Delta G°$). Table 2 presents the $\Delta G°$ values of sulfates and chlorides constituted by some of the main elements of the studied steels. It can be noted that the elements Mn, Ni, Fe and Cu have more affinity to create compounds with sulfate rather than with chloride. This could be an explanation of why Na_2SO_4 decreases the pitting corrosion in chloride containing solutions.

Table 2
Standard Gibbs free energy of formation ($\Delta G°$) of some sulfates and chlorides compounds (Weast, 1988).

Element	Sulfate Compound	$\Delta G°$ [kJ/mol]	Chloride Compound	$\Delta G°$ [kJ/mol]
Mn	$MnSO_4$	-972.78	$MnCl_2$	-490.78
Ni	$NiSO_4$	-790.35	$NiCl_2$	-259.07
Fe	$FeSO_4$	-823.49	$FeCl_2$	-299.53
Cu	$CuSO_4$	-661.90	$CuCl_2$	-175.72

It is known that the nucleation pitting mechanism has an absorption stage (Marcus, 2002 and Szklarska-Smialowska, 2005). Therefore, in the passive film, there is competitive absorption between chloride and sulfate ions (Uhlig, 1958 and Brauns and Schwenk, 1961). The differences between standard Gibbs free energy of formation found among sulfates and chlorides evidenced in Table 2 suggest that the higher Mn content of 17Cr6Mn5Ni steel thermodynamically favors adsorption of sulfate in the competitive processes. An equivalent effect was shown by Kolics *et al.,* (1998) which studied the adsorption of chloride and sulfate on pure aluminum, verifying the preferential adsorption of sulfate, which justifies the effect of pitting corrosion inhibition of sulfate in aluminum. In the same way, considering the more favorable driving force for binding between manganese and sulfate, probably the pitting inhibitory effect found for 17Cr6Mn5Ni steel is due to the increased Mn content.

It could be suggested that sulfate ions are larger than chloride ions, and even if sulfate ions are absorbed preferentially in the passive film, they do not cross the passive film, making it difficult for its breakdown. Sulfate ions kept in the passive film probably act like barriers avoiding chloride absorption and consequently avoiding pit nucleation and growth.

Concerning the effect of annealing temperature and the delta ferrite content resulted from this treatment (Figure 3), it can be concluded that pitting corrosion resistance of 17Cr6Mn5Ni steel increases with the increase of annealing temperature, if the pitting potential in the electrolytes with the highest Na_2SO_4 concentration (0.6M) are analyzed (Figure 5b). This increasing was not noticed by 18Cr8Ni steel in any electrolyte and neither by the 17Cr6Mn5Ni steel in the electrolytes containing a low Na_2SO_4 concentration (0.06M Na_2SO_4 and 0.15M Na_2SO_4). In a first analysis, this can be attributed to the combination of a higher sodium sulfate concentration and the presence of Mn in the 17Cr6Mn5Ni steel, allowing a synergetic interaction between inhibition effect of the sodium sulfate and the presence of Mn. The electrolyte with the highest Na_2SO_4 concentration is then less aggressive to the Mn content steel, and this electrolyte becomes capable of pitting potential differentiation in samples treated at different annealing temperatures.

Increasing annealing temperatures in the range studied (1010 to 1100°C) led to reduction in ferrite content of approximately 50% if compared to the N/A condition for 17Cr6Mn5Ni steel, suggesting a similar chromium enrichment in the austenitic matrix due to the dissolution of the delta ferrite islands for the studied temperatures. However, higher annealing temperatures can promote a better homogenization of the chromium gradients around the former delta ferrite islands, explaining the higher pitting potentials observed for the 17Cr6Mn5Ni steel in the less aggressive electrolyte (the one with the highest Na_2SO_4 concentration - 0.6M) with annealing temperature increase, as shown in Figure 5b. The lack of the sodium sulfate inhibition effect for the 18Cr8Ni steel did not allow the observation of this behavior (Figure 5a), although this behavior would probably be observed if a less aggressive electrolyte had been used for this steel.

5. Conclusions

Additions of Na_2SO_4 in 0.6M NaCl solution enhance the pitting corrosion resistance of 17Cr6Mn5Ni austenitic stainless steel. In different heat treatment conditions and chemical compositions of the electrolyte, 18Cr8Ni steel has a better performance than the 17Cr6Mn8Ni steel. However, in the 0.6M NaCl + 0.6M Na_2SO_4 electrolyte, 17Cr6Mn5Ni steel heat treated at 1070° C and 1100° C has a higher pitting potential than the 18Cr8Ni steel. In this less aggressive electrolytic solution, pitting corrosion resistance of 17Cr6Mn5Ni steel enhances progressively according to the increase of the heat treatment temperature from 1010°C to 1100°C, probably associated to better homogenization of the chromium gradients around the former delta ferrite islands.

Acknowledgements

References

BRAUNS, E., SCHWENK, W. Beitrag zur Kinetik der Lochfraßkorrosion an passiven Chrom-Nickel-Stählen. *Materials and Corrosion,* v. 12, n. 2, p. 73-80, 1961.

CALDERÓN-HERNÁNDEZ, J. W., HINCAPIÉ-LADINO, D., AZEVEDO, C. R. D. F., ALONSO-FALLEIROS, N. Effect of solution heat treatment on the pitting corrosion behavior of a high Mn austenitic stainless steel in chloride solution. *Rem - Revista Escola de Minas,* v. 68, n. 1, p. 91-96, 2015.

CHARLES, J. New 200 Series: an alternative answer to Ni surcharge? Dream or nightmare? In: PROCEEDINGS OF THE 5TH INTERNATIONAL EUROPEAN CONGRESS STAINLESS STEEL SCIENCE AND MARKET. Seville, Spain, September 27th-30th, 2005, p. 19-27.

CHATTORAJ, I., BHATTAMISHRA, A. K., JANA, S., DAS, S. K., CHAKRABOR-TY, S. P., DE, P. K. The association of potentiokinetic reactivation and electrochemical pitting tests on a nitrogen bearing 19 Cr-17 Mn steel with its thermal history. *Corrosion Science,* v. 38, n. 6, p. 957-969, 1996.

COLPAERT, H. *Metalografia dos produtos siderúrgicos comuns.* (4ª ed.). São Paulo: Editora Edgar Blucher, 2008. p. 11-14.

CONDYLIS, A., BAYON, F., DESESTRET, A. Aciers inoxydables austénitiques au chrome-nickel-manganèse-azote. *Revue de Métallurgie,* v. 67 p. 427-441, 1970.

GALVELE, J. R. Transport processes and the mechanism of pitting of metals. *Journal of the Electrochemical Society,* v. 123, n. 4, p. 464-474, 1976.

KEMP, M., VAN BENNEKOM, A., ROBINSON, F. P. A. Evaluation of the corrosion and mechanical properties of a range of experimental Cr-Mn stainless steels. *Material Science and Engineering: A,* v. 199, p. 183-194, 1995.

KNYAZHEVA, V. M., VEDENEEVA, M. A., ESSELDIN-HLIL, S., KOLO-TYRKIN, Y. Electrochemical study of the influence of the carbon, titanium, and manganese contents on the corrosion resistance of chromium-nickel-manganese steels. *Zashchita Metallov,* v. 1, p. 465-472, 1965.

KOLICS, A., POLKINGHORNE, J. C., WIECKOWSKI, A. Adsorption of sulfate and chloride ions on aluminum. *Electrochimica Acta,* v. 43, n. 18, p. 2605-2618, 1998.

LECKIE, H. P., UHLIG, H. H. Environmental factors affecting the critical potential for pitting in 18-8 stainless steel. *Journal of the electrochemical society,* v.113, p. 1262-1267, 1966.

LUNARSKA, E., SZKLARSKA-SMIALOWSKA, Z., JANICK-CZACHOR, M. Susceptibility of Cr-Ni-Mn stainless steels to pitting in chloride solution. *Corrosion,* v. 31, p. 231-234, 1975.

MANNING, P. E., DUQUETTE, J. The effect of temperature (25°-289°c) on pit initiation in single phase and duplex 304l stainless steels in 100 ppm c1- solution. *Corrosion Science,* v. 20, n. 4, p. 597-609, 1980.

MARCUS, P. *Corrosion mechanism in the theory and practice.* New York: Marcel Dekker, 2002.

MURGULESCU, J. G., RADOVICI, O. Über die anodische Passivierung einiger Chrom-Nickel-Mangan-Stähle bei konstantem Strom. *Zeitschrift für physikalische Chemie,* v. 214, p. 288-298, 1960

NAIR, F., SEMCHYSHEN, M. Corrosion resistance of molybdenum modified cr-ni-mn austenitic stainless steels. *Corrosion,* v. 19, n. 6, p. 210t-216t, 1963.

PARDO, A., MERINO, M. C., COY, A. E., VIEJO, F., ARRABAL, R., MATYKI-NA, E. Pitting corrosion behavior of austenitic stainless steels – combining effects of Mn and Mo additions. *Corrosion Science,* v. 50, p. 1796-1806, 2008.

RYAN, M. P., WILLIAMS, D. E., CHATER, R. J., HUTTON, B. M., MCPHALL, D. S. Why stainless steel corrodes. *Nature,* v. 415, p. 770-774, 2002.

SCHMUKI, P., HILDEBRAND, H., FRIEDRICH, A., VIRTANEN, S. The composition of the boundary region of MnS inclusions in stainless steel and its relevance in triggering pitting corrosion. *Corrosion Science,* v. 47, n. 5, p. 1239-1250, 2005.

SEDRIKS, A. J. *Corrosion of stainless steels.* (2ed.). New York: John Wiley & Sons

Inc, 1996. p. 17-21.

SHAMS EL DIN, A. M., BADRAN, M. M., KHALIL, S. E. Corrosion behavior of manganese-containing stainless steels. *Werkstoffe und Korrosion,* v. 24 p. 576-581, 1973.

SZKLARSKA-SMIALOWSKA, Z. *Pitting corrosion of metals.* Houston, TX: NACE, 1986.

SZKLARSKA-SMIALOWSKA, Z. *Pitting and crevice corrosion of metals.* Houston: National Association of Corrosion Engineers - NACE, 2005.

UHLIG, H. H. The adsorption theory of passivity and the flade potential. *Physikalische Chemie,* v. 62, n. 6-7, p. 626-632, 1958.

WEAST, R. *Handbook of chemistry and physics.* Florida: CRC, 1988. p. D55-D60.