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Effect of solution heat treatment on the pitting corrosion behavior of a high Mn austenitic stainless steel in chloride solution

Efeito do tratamento térmico de solubilização sobre a corrosão por pite do um aço inoxidável austenítico contendo alto Mn em solução de cloreto

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Abstract

The effect of solution heat treatment on the pitting corrosion resistance of 17Cr-6Mn-5Ni-1.5Cu austenitic stainless steel in 0.6M NaCl aqueous solution was evaluated. UNS S30403 (304L) steel was used as benchmark material. Solution heat treatments (SHT) were conducted at 1010°C, 1040°C, 1070°C and 1100°C. The microstructural characterization revealed the presence of δ -ferrite, especially in the as-received condition (AR). The SHT decreased the proportion of the ferrite phase. Mn-rich precipitates were observed in the as-received condition of 17Cr-6Mn-5Ni-1.5Cu steel, but they were dissolved after the SHT, causing localized Mn enrichment in the austenite. Potentiodynamic tests showed that the pitting potential (E_p) in the 304L steel was not altered significantly after SHT. On the other hand, the value of E_p of the 17Cr-6Mn-5Ni-1.5Cu steel decreased after SHT. This detrimental effect was explained by the formation of Mn enrichment areas due to the solubilization of Mn-rich precipitates, which promoted preferential Cl⁻ adsorption in these regions.

Keywords: pitting corrosion, austenitic stainless steel, 17Cr-6Mn-5Ni-1.5Cu, sodium chloride.

Resumo

O efeito do tratamento térmico de solubilização sobre a resistência à corrosão por pite do aço inoxidável austenítico 17Cr-6Mn-5Ni-1,5Cu foi avaliado em solução de 0,6M NaCl. O aço UNS S30403 (304L) foi usado como referência. Foram realizados tratamentos térmicos de solubilização (TTS) a 1010°C, 1040°C, 1070°C e 1100°C. A caracterização microestrutural revelou a presença de ferrita δ , especialmente na condição tal como recebida (TCR), observou-se que os TTS diminuíram a quantidade de ferrita. Também foram observados precipitados ricos em Mn na condição TCR do aço 17Cr-6Mn-5Ni-1,5Cu, os quais foram dissolvidos pelos TTS, causando o enriquecimento localizado da austenita em Mn. Os testes potenciodinâmicos mostraram que o potencial de pite (E_p) do aço 304L não foi alterado significativamente após TTS. Por outro lado, o valor de E_p do aço 17Cr-6Mn-5Ni-1,5Cu diminuiu após os TTS. Esse efeito detrimental foi explicado pelo enriquecimento em Mn das áreas ao redor dos precipitados dissolvidos, o que promoveu a adsorção mais

intensa de Cl- nessas regiões.

Palavras-chave: corrosão por pite, aço inoxidável austenítico, 17Cr-6Mn-5Ni-1,5Cu, cloreto de sódio.

1. Introduction

Nickel is the most important alloying element to stabilize the austenite phase in 300 series austenitic stainless steel, but its price has shown considerable fluctuations over the last decades. On the other hand, manganese (another austenite stabilizer element) has presented a more stable price over the same period. In this sense, Mn has been used to partially replace Ni in some grades of austenitic stainless steels (Charles, 2005). Prior investigations reported that Mn addition promoted a negative effect on the general corrosion resistance of austenitic stainless steels (Murgulescu and Radovici, 1960, Knyazheva *et al.*, 1965, Condylis *et al.*, 1970, Shams *et al.*, 1973, Lunarska *et al.*, 1975). All of these investigations did not propose any mechanism to explain the deleterious role of Mn addition on the general corrosion resistance of austenitic stainless steels. Kemp (Kemp *et al.*, 1995) studied the effect of Mn on general and pitting corrosion of Cr-Mn duplex stainless steels (with 3 to 10 wt.% Mn). Electrochemical tests (cyclic polarization) in 0.025N NaCl and anodic polarization in 0.1N H₂SO₄ revealed that Mn addition reduced both general and pitting corrosion resistance.

2. Experimental

The chemical composition of the investigated austenitic stainless steels is shown in Table 1. The as-received hot-rolled plates of 17Cr-6Mn-5Ni-1.5Cu and 304L austenitic stainless steels featured a thickness of 2.8 and 4.0 mm, respectively. Solution heat treatments were performed at 1010°C, 1040°C, 1070°C and 1100°C for 20 min, followed by water quenching. After the solution heat treatment, the steel plates were cut and mounted in bakelite resin. The surfaces

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 (Ryan *et al.*, 2002, Schmuki *et al.*, 2005, Pardo *et al.*, 2008). For instance, the effect of δ-ferrite on the pitting corrosion resistance of austenitic stainless steel was investigated and the results indicated that δ-ferrite had a detrimental effect on the pitting corrosion resistance, as its formation caused Cr depletion in the surrounding γ-matrix and increased the amount of δ/γ interfaces and the number of preferential pit nucleation sites (Sedriks, 1996, Manning and Duquette, 1980, Szklarska-Smialowska, 1986).

The main goal of the present investigation is to investigate the role of solution heat treatment (SHT) on the pitting corrosion behavior of the 17Cr-6Mn-5Ni-1.5Cu steel. The idea of explaining the deleterious effect of Mn addition on the pitting corrosion resistance of austenitic stainless steels merely by the presence of MnS inclusions should be questioned, especially due to the low sulfur contents found in cur-

rent stainless steels (down to 10 ppm). For instance, Pardo *et al.* (2008) stated that the number of metallic inclusions in the matrix of the stainless steel increased with Mn content, but there was no proper quantitative metallographic analysis to prove this assertion. In their discussion, the authors stated that the influence of Mn on the pitting corrosion resistance of stainless steel was not well defined, but they proposed that a higher Mn content in steel promoted the formation of a greater amount of manganese sulfides and, therefore, increased the pitting attack susceptibility of the austenitic stainless steel, independently of the sulfur content in the steel. Other possible mechanisms should be taken into account to explain the role of Mn in the pitting corrosion of stainless steels with low sulfur contents.

In the present investigation, potentiodynamic polarization measurements were carried out to evaluate the effect of solution heat treatment on the pitting corrosion resistance of 17Cr-6Mn-5Ni-1.5Cu austenitic stainless steel in chloride aqueous solution (0.6 M NaCl), while using 304L austenitic stainless steel as a benchmark material.

scanning rate of 1 mV/s. Each condition was tested at least 10 times. Additionally, the absence of crevice and the presence of pits were always verified after the electrochemical tests via optical microscopy (OM). Microstructural characterization of the transversal section of the samples was carried out in OM, scanning electron microscopes (SEM) and energy dispersive X-ray spectroscopy (EDS). The amount of δ-ferrite was quantified through a ferrite scope (FISHER MP3).

Element	C	Mn	Cr	Ni	P	Si	S	N (ppm)	Cu
UNS S30403 (304L)	0.017	1.54	18.53	8.03	0.03	0.44	0.001	483	0.05
17Cr-6Mn-5Ni-1.5C	0.029	5.82	17.17	4.64	0.03	0.32	0.002	615	1.56

Table 1
Chemical composition (wt%).

3. Results

In both steels the as-received condition shows the presence of austenitic

grains, twins and δ -ferrite. The SHT condition features larger austenite grains,

with twins and a smaller amount of δ -ferrite precipitates (see Figure 1).

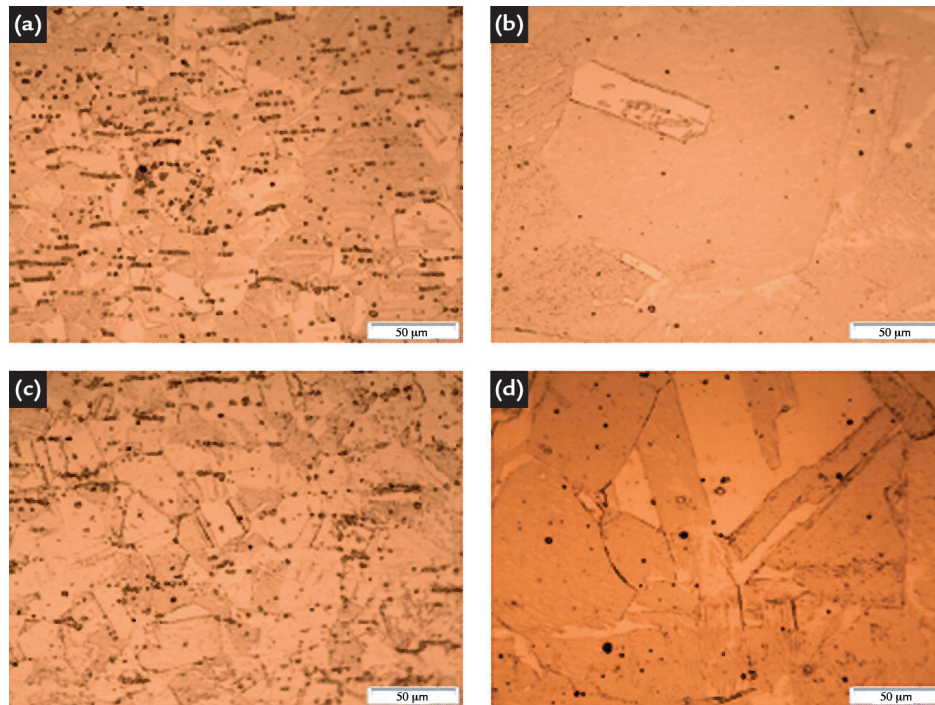


Figure 1
Microstructure of the investigated steels.

- (a) 304L steel in the as-received condition.
- (b) 304L steel heat-treated at 1100°C for 20 minutes.
- (c) 17Cr-6Mn-5Ni-1.5Cu steel in the as-received condition.
- (d) 17Cr-6Mn-5Ni-1.5Cu steel heat-treated at 1100°C for 20 minutes (electrolytic etching with 10% oxalic acid, OM).

Figures 2(a) and 2(b) show potentiodynamic polarization curves representative of values obtained for

17-Cr-6Mn-5Ni-1.5Cu and 304L steels, respectively. All curves featured well defined passive region and E_p . Figure

3 shows the graph of the E_p versus the heat treatment temperatures for all investigated conditions.

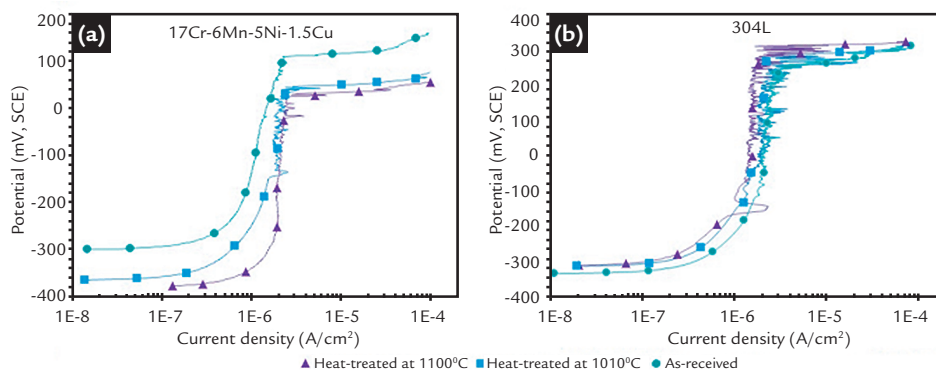


Figure 2
Representative potentiodynamic polarization curves of the steels in 0.6M NaCl solution.

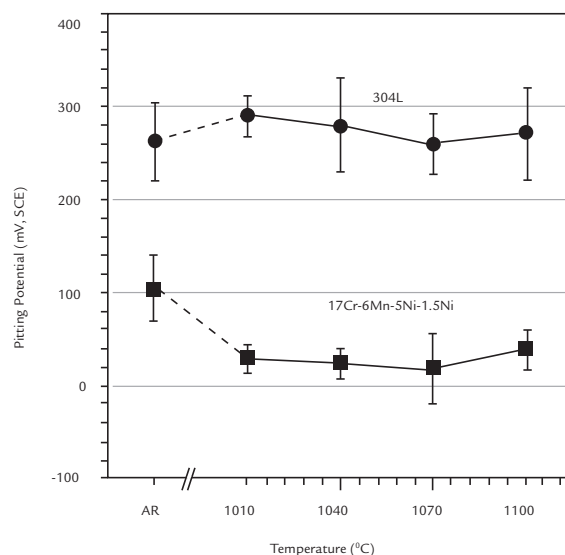


Figure 3
Pitting potential versus as-received and heat-treated conditions.

The results in Figures 2 and 3 indicate that:

- Both steels showed similar values for the corrosion potential (between -400 mV, SCE and -300 mV, SCE).
- The 304L stainless steel featured comparatively higher values (~ 200 mV) for the E_p for each one of the investigated conditions.

- The solution heat treatment schedule showed no effect on the pitting potential of the 304L stainless steel but promoted a deleterious effect on the pitting potential of the 17Cr-6Mn-5Ni-1.5Cu steel.

Microstructural characterization results are shown in Figures 4, 5 and Table 2. The Figure 4(a) shows the microstructure

of 17Cr-6Mn-5Ni-1.5Cu steel in the as-received (AR) condition with the presence of austenite and ferrite islands, while Figure 4(b) shows the effect of solution heat treatment on the amount of ferrite phase for both steels. There is a decrease in the amount of δ -ferrite from approximately 3.5% in volume (AR samples) to approximately 1.0 % in volume (SHT samples).

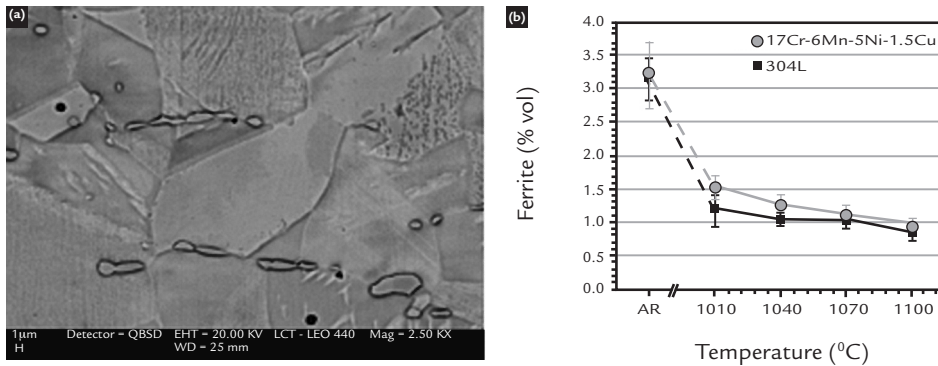


Figure 4
(a) 17Cr-6Mn-5Ni-1.5Cu stainless steel, as-received condition, austenitic matrix with δ -ferrite island (the microstructure of 304L steel was similar); (b) Volume fraction of ferrite phase using ferritescope in function of solution heat treatment temperature.

Figure 5(a) shows the presence of a Mn-rich intermetallic particle (with diameter around 2 μ m), which was only found in the as-received condition for the 17Cr-6Mn-5Ni-1.5Cu steel. The volume fraction of the intermetallic phase was

estimated to be below 1% in volume via SEM. Figure 5(b) shows the calculated Mn profile for the Mn-rich intermetallic particle after and before of SHT (1100°C for 20 minutes). This profile was calculated taking into account the size of Mn-rich

precipitate, the chemical composition shown in Table 2 and the solution for Fick's second law for a finite layer (intermetallic phase) located between two semi-infinite bodies (austenitic matrix) (Balluffi *et al.*, 2005).

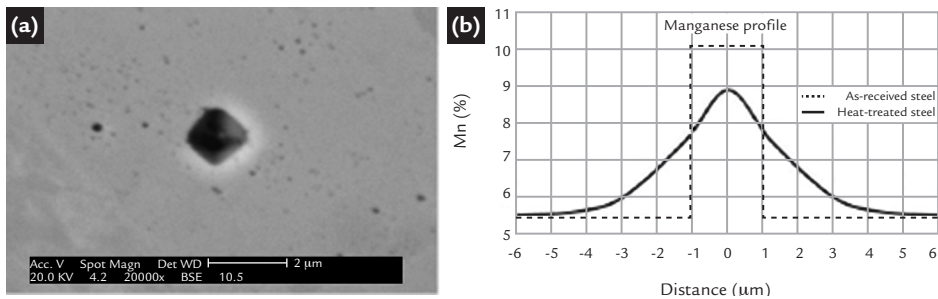


Figure 5
(a) Manganese-rich precipitate (see EDS in Table 2) found in the as-received condition of 17Cr-6Mn-5Ni-1.5Cu steel (this precipitate was not observed in the SHT conditions); (b) Mn profile after and before of SHT.

Table 2 presents the average values of the EDS results. The Mn-rich precipitate showed in Figure

5(a) contains 10.1%Mn, 3.9%Ni and 18.8%Cr. Additionally, the EDS microanalysis on the Mn-rich inter-

metallics did not show the presence of oxygen peaks.

Material	Condition	Phase	Cr	Mn	Ni
17Cr-6Mn-5Ni-1.5Cu	As-received	γ	17.0	5.9	4.9
		δ	22.5	5.2	2.7
		Mn-rich phase (Figure 4.b)	18.8	10.1	3.9
17Cr-6Mn-5Ni-1.5Cu	Heat-treated at 1100 °C	γ	16.7	5.7	4.9
		δ	22.0	5.1	2.5
304L	As-received	γ	18.9	1.8	7.8
		δ	25.1	1.6	4.4
304L	Heat-treated at 1100 °C	γ	19.0	1.5	7.7
		δ	25.2	1.4	4.1

Table 2
Average quantitative EDS results (the balance is given by iron)

4. Discussion

The solution heat treatment (SHT) affected the steel microstructure (in terms of microconstituents and the amount of interfaces) and the chemical composition of the austenite (due to the solid state dissolution of the precipitates). The dissolution of δ -ferrite with the SHT did not change the pitting potential of the 304L steel (Figures 2 and 3), in spite of the reduction in the amount of δ/γ interfaces and the possible increase in Cr content in the austenite adjacent to the dissolved δ -ferrite. This result is not in accordance with previous works, which suggested that δ -ferrite dissolution increased the pitting potential (Sedriks, 1996, Manning and Duquette, 1980, Szklarska-Smialowska, 1986). The present EDS results for the 304L steel, however, did not show any significant Cr-enrichment in the austenitic matrix caused by the δ -ferrite dissolution after the SHT (see Table 2, 304L steel).

In the case of 17Cr-6Mn-5Ni-1.5Cu steel, the SHT decreased the pitting potential (Figures 2 and 3) and the microstructural characterization showed the presence of Mn-rich intermetallic phase in the as-received condition (Figure 5), which was completely dissolved after the SHT. Additionally, the SHT showed a deleterious effect on the pitting resistance of the 17Cr-6Mn-5Ni-1.5Cu steel (Figure 3). This negative effect of the SHT might be explained by the Mn-enrichment of the austenite, which was caused by the solid state dissolution of the Mn-rich

intermetallic.

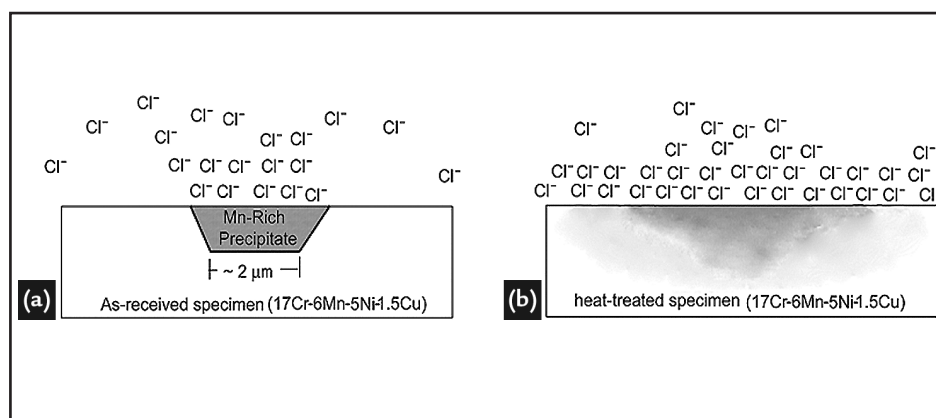
Previous works (Murgulescu and Radovici, 1960, Knyazheva *et al.*, 1965, Condylis *et al.*, 1970, Shams *et al.*, 1973, Lunarska *et al.*, 1975) showed that Mn addition exerted a detrimental effect on the passivation of austenitic stainless steels (without any further explanation) and showed a deleterious effect on the pitting corrosion of austenitic steels, due to the increase in the amount of MnS inclusions (Ryan *et al.*, 2002, Schmuki *et al.*, 2005, Pardo *et al.*, 2008). Considering that the sulfur content in current steels is 20 ppm maximum (see Table 1), there must be a limit (given by the mass balance) for the amount of MnS inclusions, which can be formed in these steels by increasing the Mn content. In this sense, the limit for the amount of MnS inclusions is defined by the amount of S in the steel and not by the amount of Mn. Other mechanisms should be considered to explain the role of Mn in the pitting corrosion of stainless steel. The present investigation proposes a thermodynamic mechanism to explain the role of solution heat treatment on the pitting corrosion of 17Cr-6Mn-5Ni-1.5Cu steel, assuming that:

- The main stage for the pitting nucleation is the Cl⁻ adsorption mechanism by the passive film.
- The adsorption of Cl⁻ in the passive film is directly associated to the thermodynamic of chloride formation, which is defined by its Gibbs free energy of formation (ΔG_f°).

There is a list of ΔG_f° values (Weast, 1988), showing that the Gibbs free energy for the formation of MnCl₂ is -491.8 kJ/mol; and that the Gibbs free energy for the formation of CrCl₂ is -356.1 kJ/mol. According to these Gibbs free energy values, the driving force for the formation of MnCl₂ is higher than that for the formation of CrCl₂, indicating that the chemical affinity between Mn and Cl⁻ is stronger than the affinity between Cr and Cl⁻.

Microstructural analyses showed that the Mn-rich intermetallic phases found in the as-received condition of 17Cr-6Mn-5Ni-1.5Cu steel - see Figure 5(a) - were completely solubilized after the solution heat treatment. Figure 5(b) showed the calculated Mn profile for the 17Cr-6Mn-5Ni-1.5Cu before and after SHT (1100°C for 20 minutes), indicating the local Mn-enrichment of the austenite. The Mn atoms of the intermetallic phase diffuse into the matrix during the SHT, forming a Mn-rich cloud in the austenite. The affinity between Cl⁻ and Mn in this cloud is higher, giving rise to preferential Cl⁻ adsorption in this region - see Figures 6(a) and 6(b). For instance, the thickness of the Mn-rich austenite presenting Mn content higher than the 6.8 wt.% of Mn is around 4 μ m. The formation larger areas of Mn-rich austenite in the microstructure after the SHT might promote more intense Cl⁻ adsorption, creating more favorable conditions for the events of pitting nucleation.

Figure 6
Sketch of the proposed mechanism to explain the role of the Mn-rich intermetallic dissolution on the pitting nucleation of 17Cr-6Mn-5Ni-1.5Cu steel in chloride solution.
(a) As-received specimen, showing the presence of a Mn-rich precipitate, diameter of $\sim 2 \mu$ m - see Figure 5(a);
(b) Heat-treated specimen, featuring the dissolution of a Mn-rich precipitate and the formation of a larger Mn-rich region in the austenite.



5. Conclusions

• The 304L austenitic stainless steel presented better pitting resistance corrosion than 17Cr-6Mn-5Ni-1.5Cu austenitic stainless steel in 0.6M NaCl solution.

• The solution heat treatment of 17Cr-6Mn-5Ni-1.5Cu steel decreased the pitting corrosion resistance.
• The 17Cr-6Mn-5Ni-1.5Cu austenitic stainless steel showed Mn-rich

precipitates in the as-received condition. The solution heat treatment dissolved these precipitates and enriched locally the austenite matrix with Mn.

• The detrimental effect of these

Mn-rich regions in the austenite on the pitting corrosion was explained by

chloride adsorption associated with the Gibbs free energy for manganese

chloride formation.

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