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Tempering effect on the localized corrosion of 13Cr4Ni0.02C and 13Cr1Ni0.15C steels in a synthetic marine environment

Efeito do revenido na corrosão localizada dos aços 13Cr4Ni0.02C e 13Cr1Ni0.15C em ambiente marinho sintético

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Abstract

Primarily, tempering is used in martensitic stainless steels with low carbon in order to change their mechanical properties. However, it also modifies the corrosion properties; usually depending on the temperature and duration of the heat treatment. This work investigated the impact of tempering on the corrosion of 13Cr4Ni0.02C and 13Cr1Ni0.15C (% weight) steels. Samples were tempered at 650°, 700° and 750°C, characterized by optical microscopy and cyclic anodic polarization tests in a synthetic marine environment. The results showed differences in the microstructure of the 13Cr4Ni0.02C tempered samples, which changed from lath to lamellar with precipitates in the prior austenite grain boundaries. On the other hand, tempering did not affect the 13Cr1Ni0.15C microstructure. The anodic polarization tests showed that the pitting potential of the 13Cr4Ni0.02C samples decreased with the tempering temperature increasing. Similar values of pitting potential were found with the 13Cr1Ni0.15C tempered samples, which were lower than the 13Cr4Ni0.02C samples after tempering. It shows that even though the corrosion resistance of the 13Cr4Ni0.02C reduces when the tempering temperature was increased, it is better than that presented by 13Cr1Ni0.15C.

Keywords: corrosion, marine environment, martensite, polarization tests.

1. Introduction

Martensitic stainless steels with low carbon concentration have been employed in hydraulic turbines, pumps and high pressure pipes in the energy and petrochemical industries (Song *et al.*, 2010; Bilmes *et al.*, 2001; Wang *et al.*, 2010; Zhang *et al.*, 2005). Usually, they are exposed to environments where the corrosion and cavitation-erosion resistances are important properties (Wang *et al.*, 2010; Gervasi *et al.*, 2011; Lai *et al.*, 2012). In the chemical composition of these steels, the chro-

mium is for increasing the corrosion resistance and the nickel, for stabilizing austenite and inhibiting delta ferrite (δ), the formation of which increases brittleness (Liu *et al.*, 2010; Balan *et al.*, 1998; Dawood *et al.*, 2004; Calliari *et al.*, 2008; Ma *et al.*, 2012).

Tempering treatments are often used to change the toughness and brittleness of this family of steels. It also modifies the microstructure. Observed alterations include a reduction in the dislocation density created during quench-

ing, microstructural transformations and nucleation of new phases or compounds (Mendonça *et al.*, 2014; Calliari *et al.*, 2008; Ma *et al.*, 2012; Park *et al.*, 2007; Choi *et al.*, 2007). Commonly, tempering also incurs the formation of chromium carbides, such as Cr_{23}C_6 , which have deleterious effects on the corrosion properties (Qin *et al.*, 2008; Sedriks *et al.*, 1996; Dexter, 2006).

The study of corrosion in a marine environment is particularly interesting for these steels because they are used in

offshore oil production facilities (Mariano *et al.*, 2007). The marine environment is complex because of the wide variety of chemical compositions, dependent on both, the geographic position and the depth. For instance, the literature (Dexter, 2006; Griffin, 2006) reports variable concentration of chlorides in marine water, which is significant because chlo-

rides increase the degradation processes of stainless steels by localized corrosion.

The influence of tempering low-carbon stainless steels on the corrosion resistance in marine environments is not well-understood, even though the importance of these steels and the microstructural transformations observed after heat treatments are well-known (Calliari

et al., 2008; Ma *et al.*, 2012; Bilmes *et al.*, 2001; Wang *et al.*, 2010). This paper presents a study that uses cyclic potentiodynamic polarization tests in a synthetic marine environment to investigate and compare the effect of tempering on corrosion for two steels with different nickel and carbon concentrations: 13Cr4Ni0.02C and 13Cr1Ni0.15C.

2. Methods

The steels were produced in an electric arc furnace with argon-oxygen decarburization (AOD). The chemical composition of the steels

in weight percentage is presented in Table 1. In order to realize the tempering, the samples were loaded into an electrical furnace (Teklabor-Model

200FM) already at the tempering temperature (650, 700 and 750°C) and removed 1 hour later to be cooled in air.

Sample	%C	%Si	%Mn	%Cr	%Ni	%Mo
13Cr4Ni0.02C	0.025	1.000	0.700	13.000	4.120	0.720
13Cr1Ni0.15C	0.153	1.020	0.750	13.000	1.030	0.080

Table 1
Chemical composition
of the samples (wt %).

The microstructure of the tempered samples was characterized using optical microscopy, and surface etching was achieved with modified Behara (0.2 l/HCl + 1l/H₂O + 1g/K₂S₂O₃) at room temperature.

Corrosion behavior was evaluated using a replicated electrochemical cyclic potentiodynamic polarization method. The electrodes were produced from stainless steel sheets, machined in

cylindrical forms (base area: 0.5 cm²), insulated with a slow-cure epoxy resin to prevent the formation of air bubbles at the resin-metal interface.

In preparation for the tests, all samples were polished mechanically with grade 600 SiC sandpaper, rinsed in alcohol and dried. Two measurements were taken at room temperature (25°C) for each sample with a model Autolab/PGSTART302 potentiostat-

galvanostat device, using a conventional three-electrode cell. A saturated calomel electrode (SCE) was used as a reference electrode for the tests, while a Pt plate was employed as counter-electrode. The potentiodynamic curves were measured at a potential scan rate of 1 mV/s in a synthetic seawater environment prepared according to ASTM D 1141. The standard chemical composition of the seawater is presented in Table 02.

Compound	Concentration, g/L
NaCl	24.530
MgCl ₂	5.200
Na ₂ SO ₄	4.090
CaCl ₂	1.160
KCl	0.695
NaHCO ₃	0.201
KBr	0.101
H ₃ BO ₃	0.027
SrCl ₂	0.025
NaF	0.003

Table 2
Chemical composition
of the synthetic seawater.

3. Results and discussion

3.1. Influence of tempering on the microstructure

Figure 1 shows the microstructure of the tempered 13Cr4Ni0.02 steel at three different temperatures. In the sample tempered at 650°C (Figure 1(a,b)), the typical martensitic structure of low-carbon steel with laths and the delta ferrite as previously found by Mariano *et al.* (2007) are observed. In the sample tempered at 700°C, the matrix is similar to the one in the sample tempered at 650°C,

martensite laths and delta ferrite (Figure 1(c,d)). On the other hand, the sample tempered at 750°C presented a different matrix, with a lamellar morphology, delta ferrite and precipitates in the prior austenite grain boundaries (Figure 1(e,f)). According to Bilmes *et al.* (2001) and Song *et al.* (2010), this latter microstructure, with austenite in the grain boundaries and lamellae, is the result of martensite

decomposition, at temperatures slightly under the austenitization temperature by diffusion processes. Furthermore Bilmes *et al.* (2001) proposed that the tempered microstructure is composed of tempered martensite, carbides and austenite. Equations (1) and (2) represent the reaction where martensite could become austenite (1) and/or ferrite (2). Both equations also indicate carbides formation.

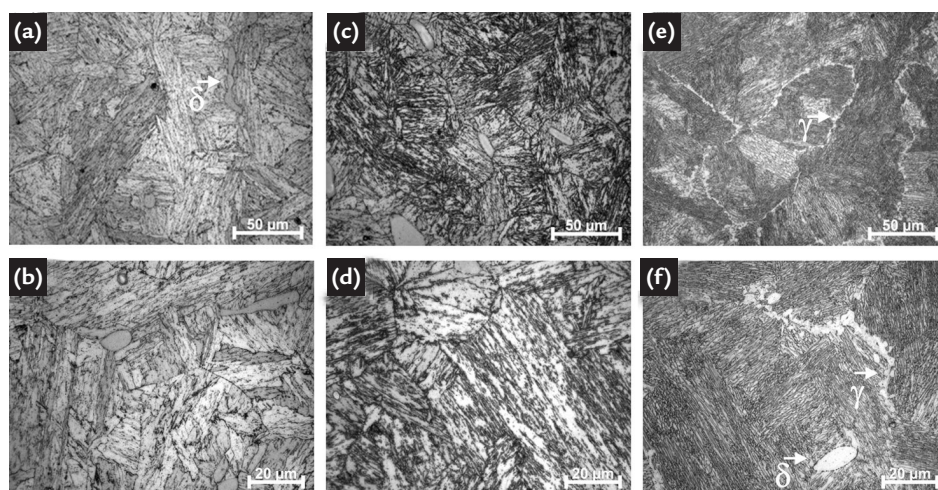
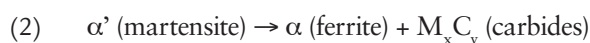
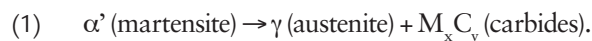


Figure 1
Microstructure of the
13Cr4Ni0.02C samples tempered at
650°C (a,b), 700°C (c,d) and 750°C (e,f).

By comparison, Figure 2 presents the microstructures of the 13Cr1Ni0.15C samples after tempering. The morphology observed is similar in all tempered samples: delta ferrite in a martensitic matrix is observed and there

is no evidence of a tempering effect on the microstructure. The relatively low concentration of Ni is considered a crucial point in this result because it is the element employed to stabilize the austenite and is reported to facilitate reverse

austenite formation in martensitic steel (Song *et al.*, 2010; Bojack *et al.*, 2012). Therefore, it is probable that the lower amount of Ni in the 13Cr1Ni0.15C samples would limit this steel's ability to present reverse austenite.

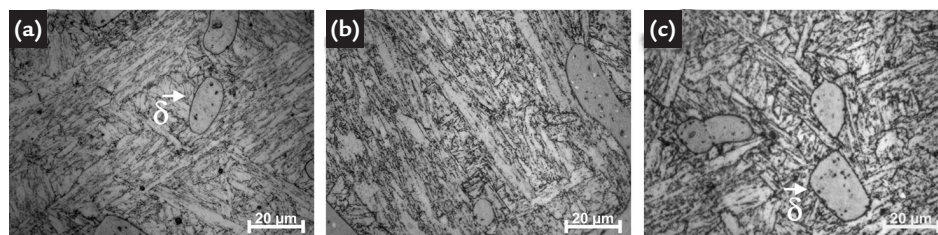


Figure 2
Microstructure of the
13Cr1Ni0.15C samples tempered at
650°C (a), 700°C (b) and 750°C (c).

3.2. Influence of tempering on cyclic anodic polarization curves

Cyclic polarization curves are shown in Figure 3. The presence of closed cycles indicates pitting corrosion on the samples which were visually confirmed after the tests. Thompson and Payer (1998) discussed in details the cyclic anodic polarization curves and pointed out that, during reversion of the potential, active pits formed in the transpassive region can further increase the current density preventing the overlap of the

points on the curve and providing the hysteresis loop. The curves show similar values for the corrosion potential (E_{CORR}) - potential of a corroding surface in the electrolyte - and different values for the pitting potential (E_{PIT}) - the lowest value of oxidizing potential at which pits nucleate and grow - as summarized in Table 3 and indicated in the Figure (3a).

The tempered 13Cr4Ni0.02C samples have similar E_{CORR} values.

However, the results of E_{PIT} are distinct; the highest value is from the sample tempered at 650°C. The values of protection potential (E_{PROT}) - the most noble potential where pitting corrosion will not propagate - show a significant difference for the sample tempered at 750°C. This result indicates that the repassivation process on this surface is slower and consequently it is more susceptible to corrosion. In contrast, for the

13Cr1Ni0.15C samples, the E_{PIT} values are similar, and the instability of the current close to the E_{PIT} (Figure 3) indicates

the formation of metastable pits that are quickly passivated during the tests of the 13Cr1Ni0.15C samples. The E_{PROT} values

can be considered similar because the spread is lower than 50 mV (Thompson and Payer, 1998).

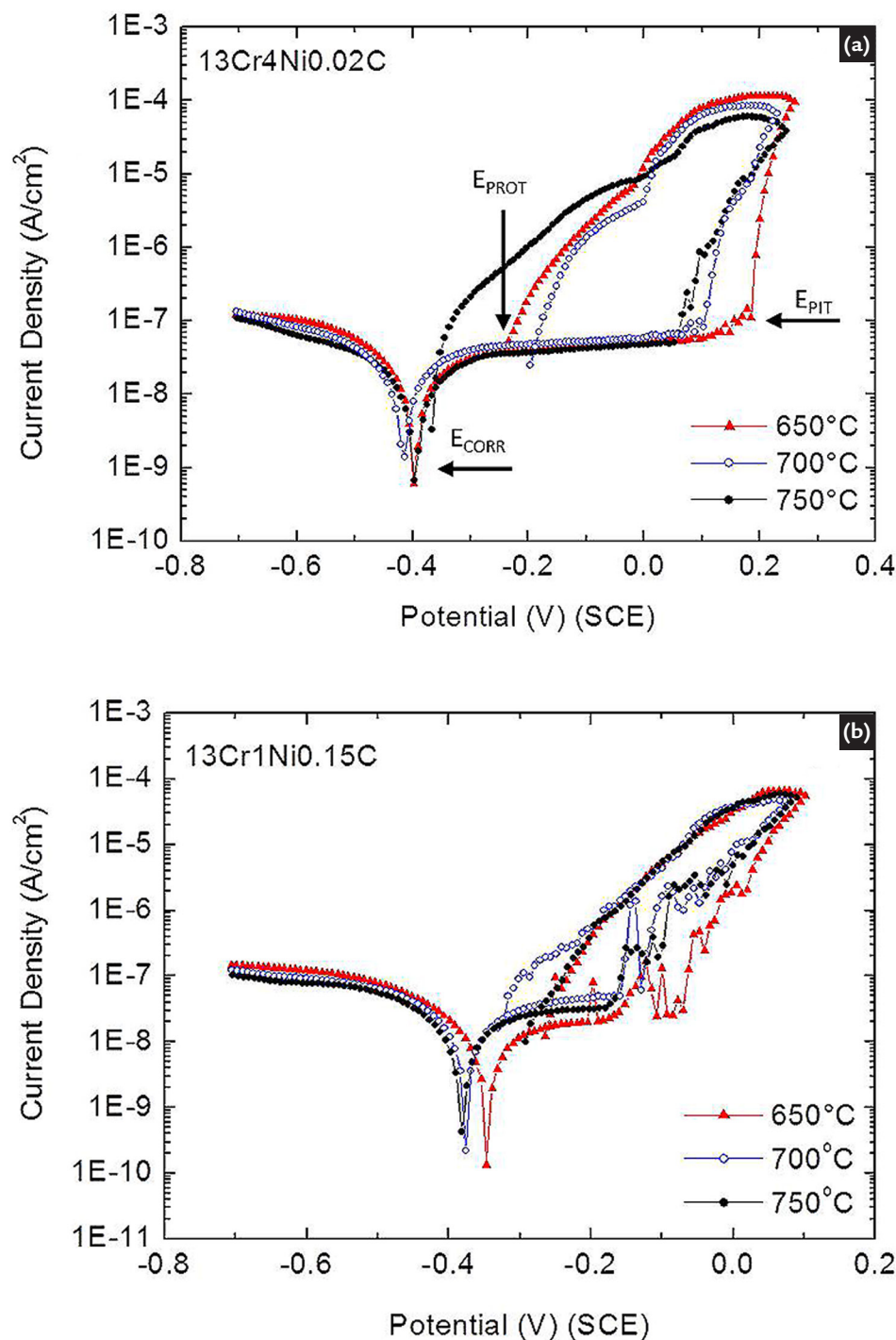


Figure 3
Cyclic anodic polarization curves for 13Cr4Ni0.02C (a) and 13Cr1Ni0.15C (b) after tempering at 650°, 700° and 750° C.

The different morphology exhibited by the 13Cr4Ni0.02C sample tempered at 750°C is related to its lower E_{PIT} values and consequently to its low corrosion resistance. Influenced by high Ni concentration and characterized by the martensite changes, the phase transformations indicate the complex carbide formation in these steels that are associated with low corrosion resistance (Gervasi *et al.*, 2011; Qin *et al.*, 2008). Previous works (Song *et al.*,

2010; Tabatabae *et al.*, 2011; Ma *et al.*, 2012; Camillo *et al.*, 2010) showed that the formed carbides could cause localized chromium depletion, changing the corrosion properties of low-carbon martensitic steels.

The 13Cr4Ni0.02C sample tempered at 700°C presented no important change in the observed microstructure but showed a lower E_{PIT} . It suggests that transformations which are not noted in the microstructure, such as carbide

precipitation, occur and change the corrosion resistance.

Comparative analysis of the cyclic polarization curves of the two tempered steels shows similar E_{CORR} but a different E_{PIT} . Lower values of the pitting potential show that the 13Cr1Ni0.15C tempered steels are more susceptible to corrosion in marine environments. This susceptibility is mainly due to the molybdenum and carbon compositions: molybdenum plays a role in the growth

of a stable passive oxide, preventing the pits formation; and carbon increases the propensity for the formation of chromium carbides related to the lower corrosion (Grubb *et al.*, 2005). The

mechanism used to understand the carbide effect is connected with the affinity of chromium to carbon, producing chromium carbides and decreasing the amount of dissolved chromium, which

is fundamental in passivation. The chromium carbide formation creates regions depleted in dissolved metallic chromium and consequently susceptible to localized corrosion.

	650°C	700°C	750°C	650°C	700°C	750°C
	13Cr4Ni0.02C			13Cr1Ni0.15C		
E_{CORR} (mV)SCE	-395.1±20.0	-415.3±21.0	-395.1±20.0	-347.9±17.5	-375.7±19.0	-385.5±19.5
E_{PIT} (mV)SCE	189.0±10.0	10.4±20.0	5.0±15.0	160.3±20.6	157.9±16.0	170.6±17.0
E_{PROT} (mV)SCE	- 245.8	- 192.8	- 359.4	- 261.6	- 322.4	- 277.5

Table 3
Potential Corrosion (E_{CORR}), Pitting Potential (E_{PIT}) and Protection Potential (E_{PROT}) obtained from the polarization curves.

4. Conclusions

In summary, the corrosion of tempered 13Cr4Ni0.02C and 13Cr1Ni0.15C steels was investigated by means of electrochemical cyclic potentiodynamic polarization in a synthetic marine environment.

Tempering at 750°C for 1 hour clearly modified the 13Cr4Ni0.02C steel microstructure. Typical martensitic microstructure constituted of laths became

lamellar due to the nickel concentration that induces the formation of austenite. This lamellar microstructure of the 13Cr4Ni0.02C steel demonstrated lower pitting potential in marine environments and consequently reduced corrosion resistance.

On the other hand, the 13Cr1Ni0.15C steel did not present significant microstructural or changes in

the pitting potential, and consequently in the corrosion resistance, with increasing of the tempering temperature.

The comparison of the pitting potential values of the two tempered steels shows that the corrosion resistance of 13Cr4Ni0.02C steel is better than 13Cr1Ni0.15C steel, mainly due to difference in the carbon and molybdenum concentrations.

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