Evaluation of Critical Pitting Temperature for Superduplex Stainless Steel

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Introduction

Superduplex stainless steels are special alloys that present two distinct phases, austenite and ferrite, in approximately equal fractions. These materials correspond to a favorable combination of mechanical properties and corrosion resistance. Superduplex steels are generally used in applications that require a high mechanical resistance in severe corrosive environments, such as paper production, oil tankers, desalination, chemical processes and petroleum industry, where the conditions are favorable to the pitting corrosion.

Although this type of material has a high pitting corrosion resistance at low temperatures (near 25°C), when used in more severe processes, as high pressures and/or temperatures, pitting corrosion can occur. To evaluate the influence of the temperature on pitting corrosion it is necessary the determination of the temperature where the pitting nucleation occurs, called critical pitting temperature (CPT).

The ASTM (American Society for Testing and Materials) regulates the determination of CPT and pitting resistance for common stainless steels. However, the ASTM-G150 and ASTM-G48 norms when used for superduplex steels, do not show reliable results.

The objective of this study is to determinate the CPT for the superduplex steel using the two cited standards with different techniques and forms of assessment, in order to get closer to a more refined and realistic result.

Experimental

Electrolyte: 6% $FeCl_3.6H_2O$ + 1% HCl solution. Working electrode: superduplex stainless steel (N 4501), machined into cylinders of 0.6 cm diameter, attached to brass rods for electrical contact and embedded in acrylic resin. Before electrochemical analysis, the electrodes were abraded with sandpaper 100, 220, 320, 400 and 600 mesh, washed with distilled water and ethanol and then dried with hot air blast. It was used a conventional electrochemical cell of three-electrodes. A large area platinum plate was used as counter electrode, and a saturated calomel electrode (SCE) as reference.

The electrochemical tests were performed on an Autolab PGSTAT 30 (Autolab Electrochemical Instruments, Eco Chemie, Netherlands).

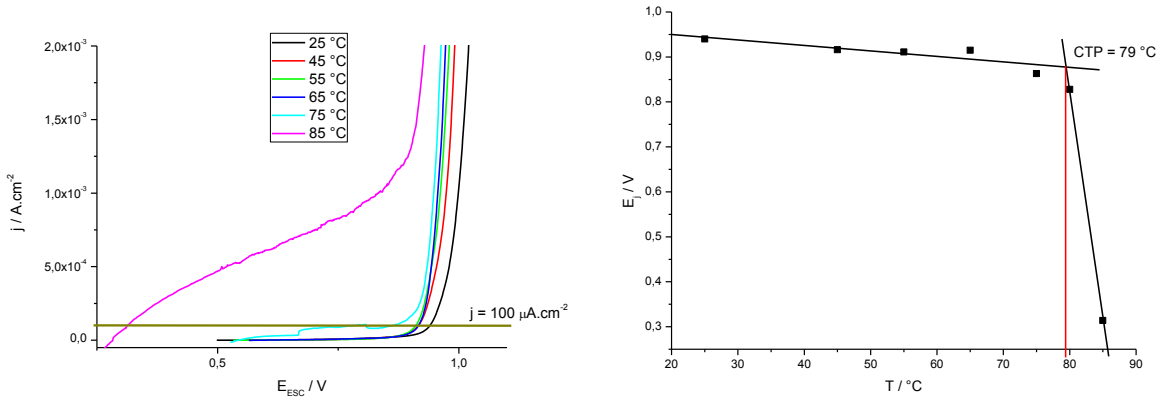
The polarization measurements were made after two hours at OCP, to attain the corrosion potential, E_{corr}. The curves were registered from E_{corr} to 1.075 V vs SCE, at different temperatures, with 1 mVs^{-1} scan rate.

The chronoamperometric curves were obtained at a predetermined potential from polarization curves (600, 700 and 800 mV vs SCE), during 30 minutes at each potential.

The micrographies were obtained in a machine model JSM – 7401 F – Field Emission Scanning Electron Microscope. The images were obtained on the surface of a sample previously polished with diamond paste to 1 μm, immersed in the study solution, polarized at 0.800 V for 30 minutes, then washed and dried.

Results and Discussion

The first attempt to determine the CPT was made from the potential value (E_i) of current increasing, or, as can be seen in Figure 1a, choosing a current density value, indicated by G-150 standard (100 $\mu A.cm^{-2}$), and plotting the results of potential as a function of the temperature, on Figure 1b. The CPT values were determined from the intersections of the extrapolated lines.

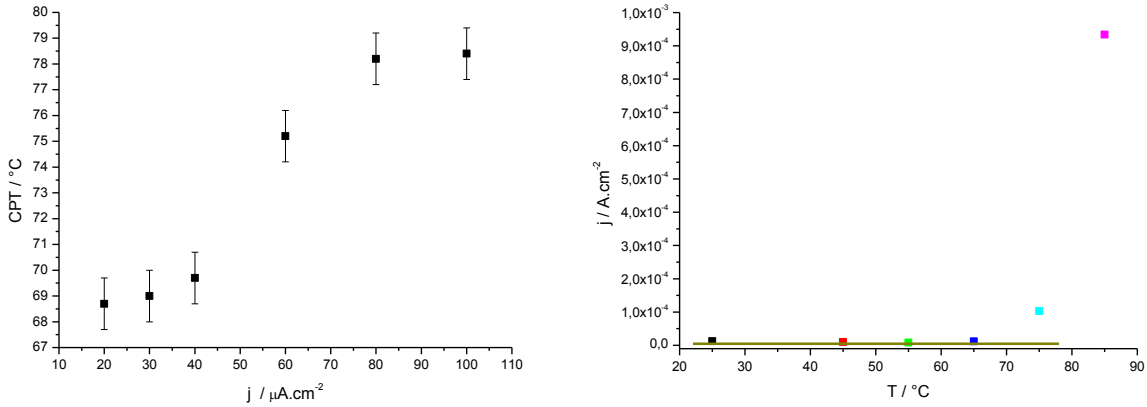


(a) (b)

Figure 1: Determination of (a) E_i by polarization curves obtained in 6% $FeCl_3.6H_2O$ + 1% HCl medium, (b) the CPT graphic; taken the limiting current density of 100 μA.cm^{-2}, as described by ASTM.

It can be seen from Figure 1b that the CPT is 79 °C. If the polarization curves are observed more closely, it can be noted that the curve obtained at 75 °C in the passive region has a current density greater than those observed for the curves obtained at lower temperatures. This may be an indicative of some type of attack is occurring on the surface at a temperature below 80 °C. It can be seen from Figure 1a that the potential E_i depends on the choice of the value of the current density, affecting the critical pitting temperature.

Figure 1a corresponds to different current density values used to obtain Ei. Figure 2b presents the current densities as a function of the temperature when the potential is equal to 0.800 V.



(a) (b)

Figure 2: (a) Determination of CPT considering different current densities (b) graph of current density versus temperature, at 0.8 V.

In the Figure 2a is noted that the CPT acquires a constant value, within experimental error, (69±1 °C) between 40 and 20 μA.cm^{-2}. In the Figure 2b is noted that at 75 °C occurs a significant increase in current density, indicating the presence of another process that may be the nucleation of the pitting. When the results of Figure 2a and 2b are compared, it is noted that, for the two different approaches, the pitting is occurring at lower temperatures than the CPT previously determined.

Figure 3 shows the results of chronoamperometry at 75 °C, a temperature between the two different CPT values.

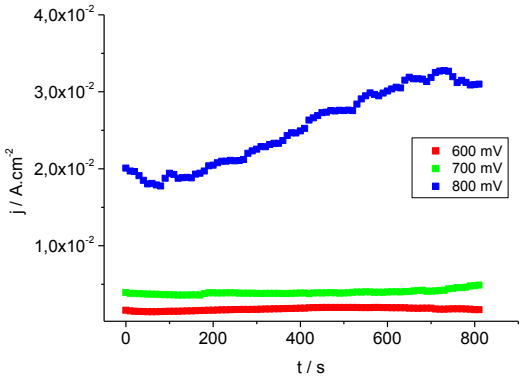


Figure 3: Chronoamperometric tests performed at 75 ° C in three different potentials.

The results obtained from chronoamperometry indicate that at 0.800 V, the current density is not constant, suggesting pitting corrosion. This can be confirmed in Figure 4 where the microscopic analysis, made under the same conditions, clearly demonstrates the formation of pitting.

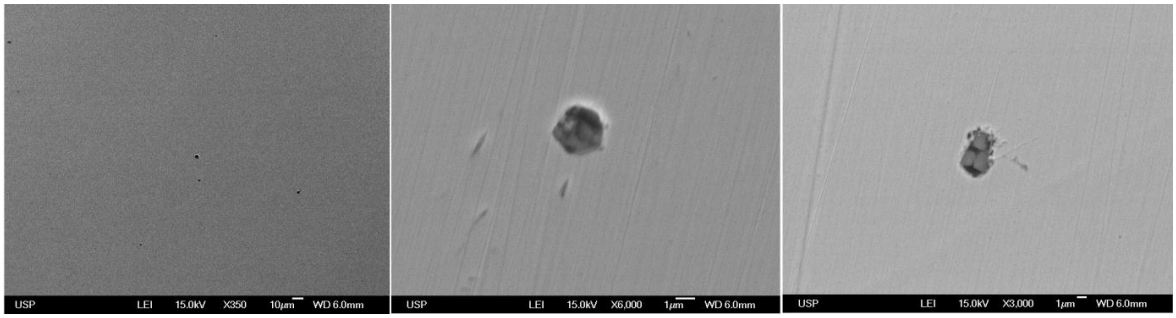


Figure 4: Microscopy made on the superduplex steel surface N4501 after 30 minutes of soaking in $FeCl_3.6H_2O$ 6% + 1% HCl, under 0.8 V, with different magnifications.

It was possible from polarization curves to get two different values of CPT: 79 °C when it was used the current density of 100 µA.cm^{-2}, and 69 °C when considered lower current densities, between 20 and 40 µA cm^{-2}. It can be argued that the highest value of CPT found is not reliable because the cronoamperometric and microscopic results denote that there is the formation of pitting at 75 °C.

Conclusions

It was possible to reach more reliable and realistic results of CPT for superduplex stainless steel from ASTM standards applied to conventional stainless steels. The CPT was better evaluated using: different values of current densities to obtain the potential where the passivated film is not present in the surface; plotting the current density as a function of the temperature at a constant critical potential; using cronoamperometry and microscopic techniques to confirm the presence of pits.

Acknowledgements

Villares Metals and CNPq.

References

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