

## An Electrochemical Study of the Corrosion Behavior of a Dual Phase Steel in 0.5M H<sub>2</sub>SO<sub>4</sub>

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This paper reports the effect of heat treatment on the corrosion resistance of a dual phase steel in 0.5M H<sub>2</sub>SO<sub>4</sub> at 60°C using weight lost, potentiodynamic polarization curves, electrochemical impedance spectroscopy and electrochemical noise measurements. Heat treatments included tempered at 750° C, quenched in water at either 0 or 40 ° C or with forced air; after this, steel was annealed at 250 and 400 ° C. Results showed that with increasing the martensite percentage in the specimen and the ferrite percentage decreases the corrosion rate decreased. In all cases, regardless of the cooling media or the annealing temperature, the corrosion process was under charge transfer and diffusion of aggressive species through the corrosion products layer. For specimens quenched in water, the susceptibility to localized type of corrosion decreased by increasing the annealing temperature. The steel cooled with forced air was always susceptible to localized type of corrosion regardless of the heat treatment.

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**Keywords:** Dual steel, corrosion, heat treatment

### 1. INTRODUCTION

Over the last two decades, a big effort on the development of new steels with better mechanical properties such as ductility and yield strength has been investigated [1-3]. The demand of such type of steels is mainly attributed to the automotive [4], army [5] and naval industry [6].

During the 70's energy crisis, a new kind of steels named "Dual phase steels" (DP) was discovered. This type of steels showed a microstructure made mainly of ferrite and martensite [7]. They had a higher ultimate tensile strength value and better ductility than traditional High Strength

Low Alloy Steels (HSLA) [8]. Since then, DP steels have a lower density than HSLA steels and have become very important in the automotive industry. They improve the fretting fatigue properties of some car parts [8-10]. DP steels have become very important for structural purposes [11-13] as well as in the low temperature pipes [14], especially steels with a ferrite-bainite structure where martensite has been substituted by bainite in order to increase their hardness level by some appropriated heat treatments.

These steels have shown some corrosion resistance according to their chemical composition. For instance, according to the carbon contents, their corrosion resistance increases or decreases; with low carbon levels, the presence of carbides is avoided and the corrosion resistance is improved since the presence of micro galvanic cells is avoided. This corrosion resistance can be also due to a better phase distribution, since the resulting microstructure after a heat treatment such as quenching provides ferrite surrounding martensite islands. By increasing silicon contents allows the formation of a SiO<sub>2</sub> passive layer which is corrosion resistant [15].

Works concerning the corrosion resistance of dual phase steel are very limited [16-20] but most of the studies are devoted to the corrosion resistance of mild steel [21-24] and, generally speaking, they possess good corrosion resistance. For instance, Sarkar et al. [17] evaluated the galvanostatic corrosion behavior of five different DP steels by changing morphologies and martensite contents in comparison with ferrite-pearlite steel in 3.5% NaCl solution. They found that both the amount of martensite and the morphology of the phase constituents have a marked influence on the corrosion behavior of the DP steel, with a higher corrosion tendency as the amount of martensite decreased and by increasing the refinement of phase constituents. Sulfuric acid is an environment commonly found in industry, for this reason, it is necessary to carry out a systematic study on the effect of microstructure on the corrosion resistance of a newly developed dual phase steel in a common environment found such as H<sub>2</sub>SO<sub>4</sub>.

## 2. EXPERIMENTAL PROCEDURE

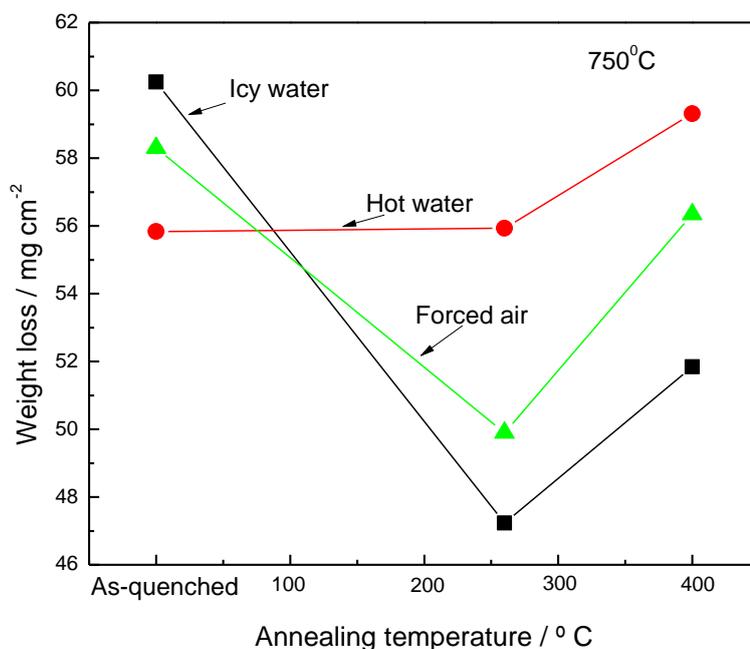
The used dual-phase steel was elaborated using vacuum induction furnace under an inert atmosphere. Chemical composition is given on table 1.

**Table 1.** Chemical composition of used steel (wt.%)

C	Si	Mn	P	S	Ni	Al	Co	Cu	Nb	Fe
0.085	0.034	1.5	<0.000	<0.000	0.012	0.054	0.007	0.032	0.033	bal

Semi-rolled slabs were heated at 750° C during 60 minutes, and then quenched either in water + ice, in hot water (40°C) or with forced air. Finally, specimens were annealed either at 260 or 400° C during 5 minutes and then air cooled. In the as-received state, the steel microstructure consists of equiaxed martensite regions with some fine pearlite regions observed. Since different amounts of

martensite and pearlite were obtained with the different heat treatments, the volume fraction of the different phases were measured by the point-counting technique following ASTM E 562-02 standard [25] using an image analyzer attached to an optical microscope. Corrosion rate was determined by conducting conventional weight loss measurements in 0.5M H<sub>2</sub>SO<sub>4</sub> at 60° C during 1 h by triplicate. Specimens used for the weight loss tests were 10 mm X 10 mm X 2 mm. After corroded, specimens were cleaned with 30 g of Sb<sub>2</sub>O<sub>3</sub> + 50 g of SrCl<sub>2</sub> in 773.77 ml of HCl at 60°C during 5 minutes. Electrochemical techniques employed included potentiodynamic polarization curves, electrochemical impedance spectroscopy, EIS and electrochemical noise, EN, measurements. Measurements were obtained by using a conventional three electrodes glass cell with a graphite rode and a saturated calomel electrode (SCE) as reference. Polarization curves were recorded at a constant sweep rate of 1 mV/s at the interval from -300 to +2000 mV<sub>SCE</sub> respect to the open circuit potential, E<sub>corr</sub>. Electrochemical impedance spectroscopy tests were carried out at E<sub>corr</sub> by using a signal with amplitude of 10 mV<sub>SCE</sub> and a frequency interval of 0.1 Hz-30 kHz. Finally, electrochemical noise measurements, EN, in current were recorded using two identical working electrodes. EN measurements were carried out by recording current fluctuations at a sampling rate of 1 point per second for a period of 1024 seconds. A fully automated zero resistance ammeter (ZRA) from ACM instruments was used in this case. Removal of the DC trend from the raw noise data was the first step in the noise analysis. To accomplish this, a least square fitting method was used. An ACM potentiostat controlled by a desk top computer was used for the polarization curves, whereas for the EIS measurements, a model PC4 300 Gamry potentiostat was used. The surface morphology of the different specimens after the corrosion tests were taken with a scanning electronic microscope (SEM).

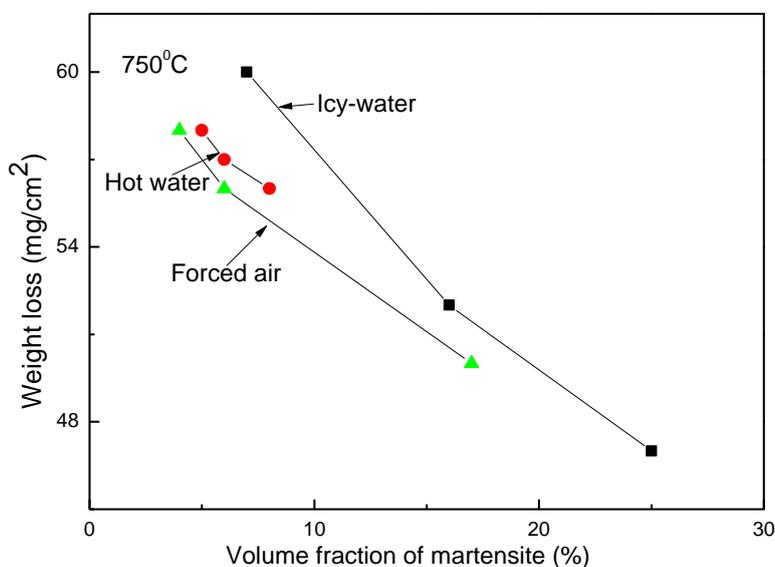


**Figure 1.** Effect of the annealing temperature on the weight loss value for a dual phase steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 60 °C, cooled in different media.

### 3. RESULTS AND DISCUSSION

#### 3.1. Weight loss measurements

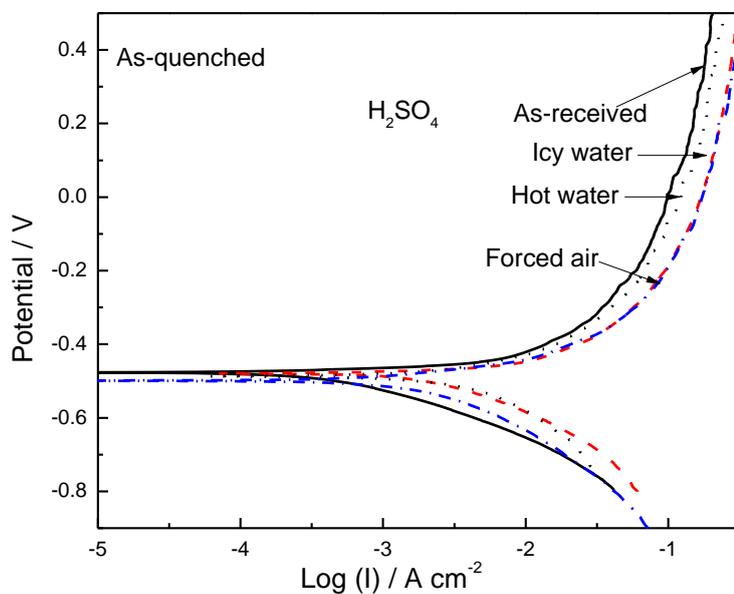
Fig. 1 shows the effect of annealing temperature on the weight loss for specimens tempered at 750°C and quenched in different media. In general terms, the as quenched specimens had the highest corrosion rate values, then the degradation rate decreases when they are annealed at 260°C, with an increase in the weight loss value with a further increase in the annealing temperature at 400°C. For the as-quenched condition, the highest corrosion rate value was exhibited by the specimen quenched in icy water, whereas the lowest corrosion rate was for the steel quenched in hot water. However, for specimens annealed either at 260 or 400°C the opposite was observed: the lowest corrosion rate was for the steel quenched in icy water whereas the highest degradation rate was for specimen quenched in hot water. Thus, in order to explain this behavior apparently erratic, the corrosion rate, expressed in terms of the weight loss value was plotted as a function of the volume fraction of martensite, as shown in Fig. 2.



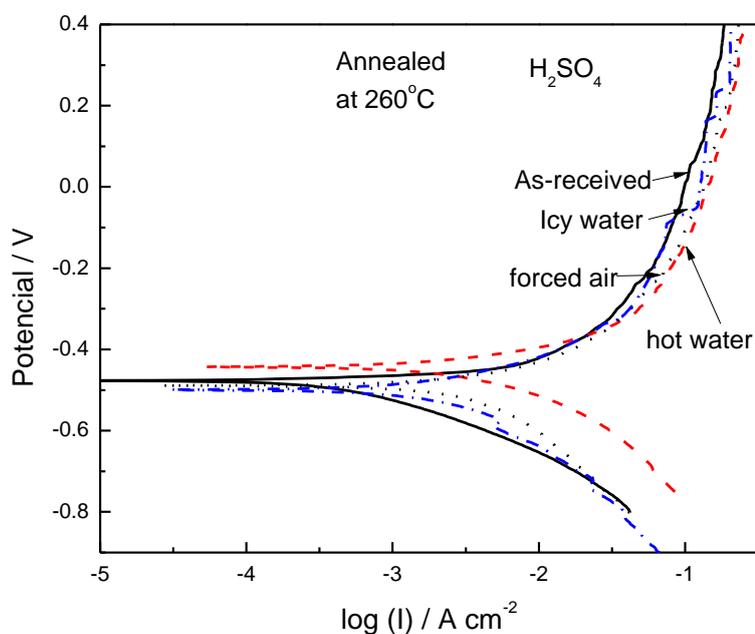
**Figure 2.** Variation of the weight loss value with the volume fraction of martensite for a dual phase steel cooled in different media.

It is very clear that, regardless the cooling media, the corrosion rate of the steel decreases as the volume fraction of martensite increases, i.e. the volume fraction of ferrite increases, although this effect is more pronounced for specimens quenched in icy water or with forced air, and much less evident for steel cooled in hot water. This behavior has been attributed to the fact that ferrite, with more Fe contents than martensite, acts as anode whereas martensite, with a higher C contents than ferrite, acts as a cathode.

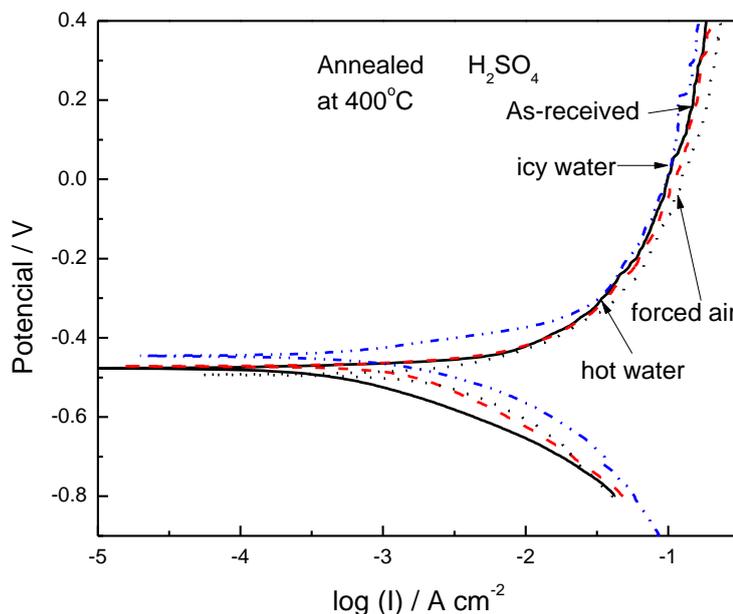
Polarization curves for the different specimens cooled in the different media are shown in Figs.3-5. The effect of cooling media on the polarization curves for the as-quenched specimens, together with the as-received steel, is shown in Fig. 3.



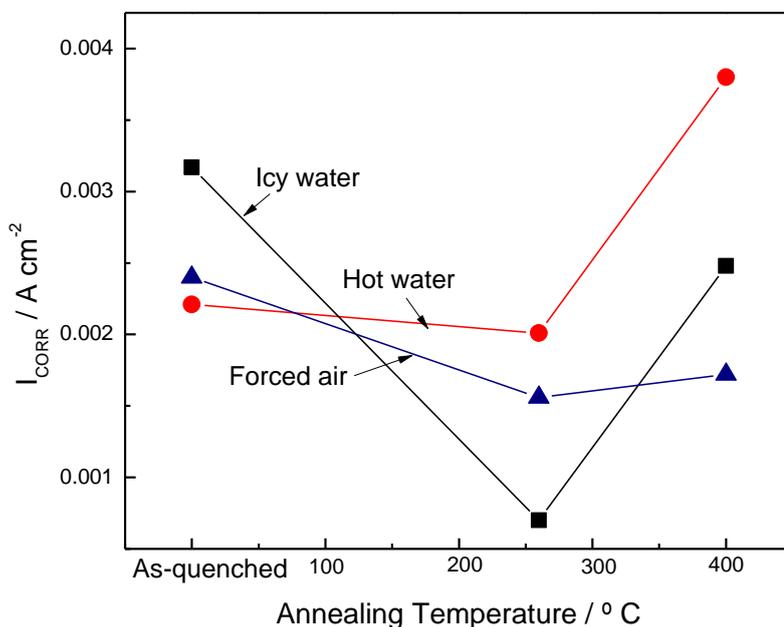
**Figure 3.** Effect of the cooling media on the polarization curve in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 60 °C, for the dual phase steel in the as-quenched condition.



**Figure 4.** Effect of the cooling media on the polarization curve in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 60 °C, for the dual phase steel quenched and annealed at 260°C.



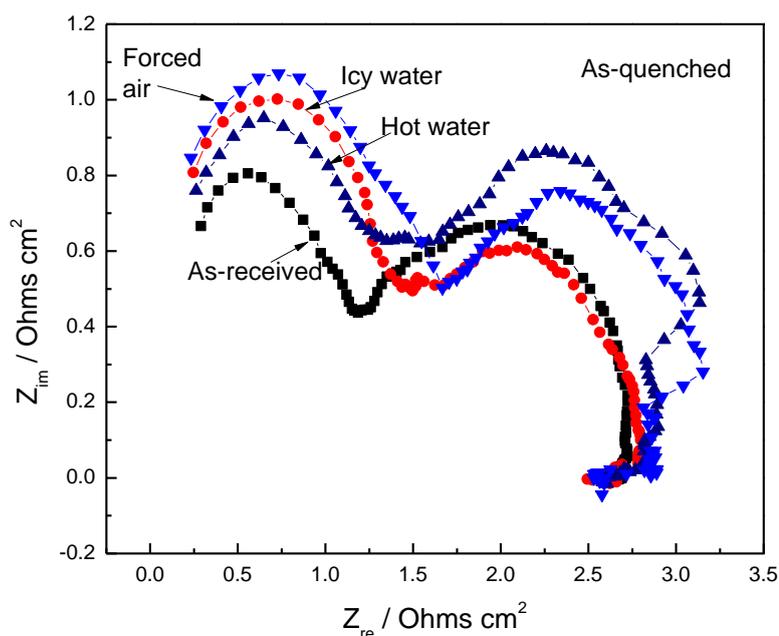
**Figure 5.** Effect of the cooling media on the polarization curve in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 60 °C, for the dual phase steel quenched and annealed at 400°C.



**Figure 6.** Effect of the annealing temperature on the I<sub>corr</sub> value for a dual phase steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 60 °C, cooled in different media.

In all cases, the curves exhibited an active behavior only, without evidence of a passive layer. Instead, the curves showed a limiting anodic current density, indicating that the electrolyte has to diffuse through a layer of corrosion products, which makes more difficult the access of the aggressive ions to the metal, protecting some how the underlying metal. The E<sub>corr</sub> values were very close to each

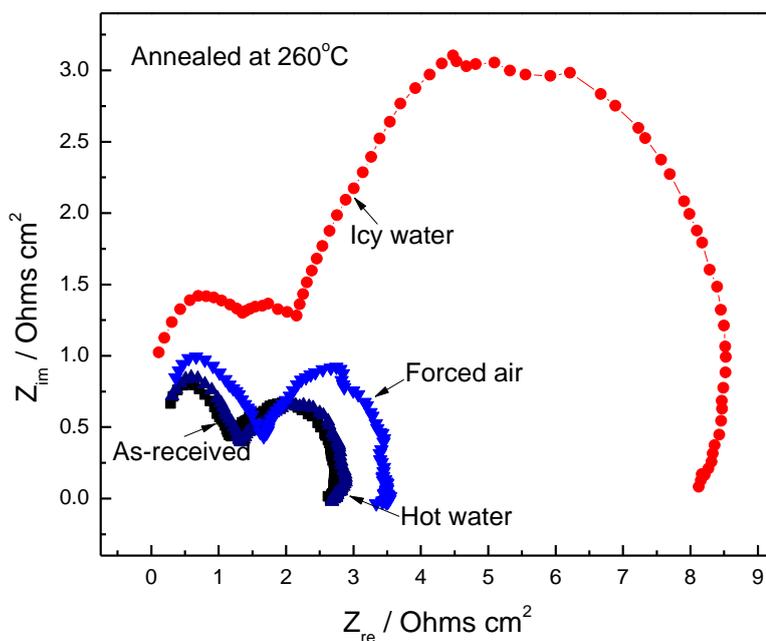
other, within -450 and -500 mV, whereas the corrosion current density value,  $I_{\text{corr}}$ , was highest for steel quenched in icy water, and the lowest value was for specimen cooled in hot water. The corrosion rate, expressed in terms of  $I_{\text{corr}}$ , was lowest in all cases, for the as-received steel. For the steel annealed either at 260 or 400°C, Figs.4-5, this behavior was the opposite, similar to that observed by the weight loss values shown on Fig. 1: the lowest  $I_{\text{corr}}$  value was for the steel cooled in icy water, whereas the highest corrosion rate was for specimen cooled in hot water, as can be seen on Fig.6, which shows the change in the  $I_{\text{corr}}$  value as a function of the annealing temperature for specimens quenched in the different media. We can see that, in general terms, regardless the cooling media and the annealing temperature, the corrosion rate exhibited by the steel in the as-received condition was lower in all cases.



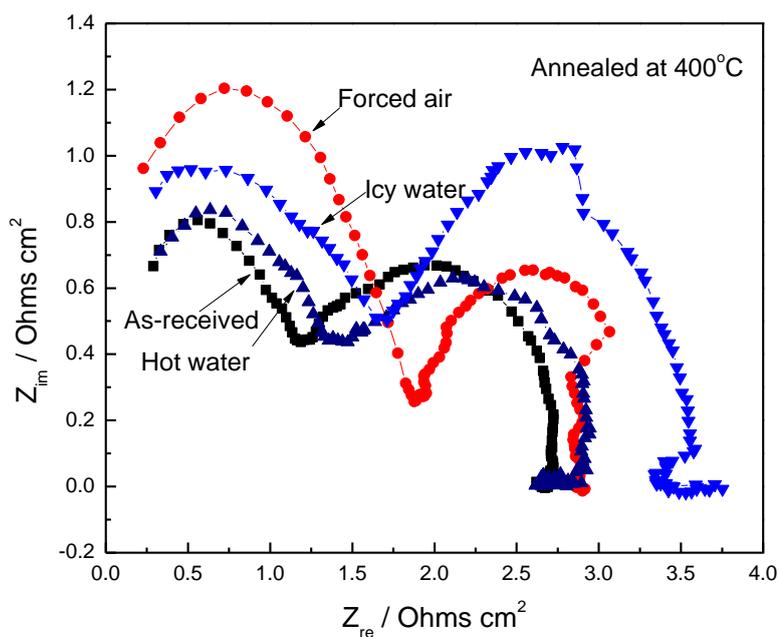
**Figure 7.** Effect of the cooling media on the Nyquist diagrams in 0.5 M  $\text{H}_2\text{SO}_4$ , 60 °C, for the dual phase steel in the as-quenched condition.

The effect of quenching media in the Nyquist diagrams in 0.5M  $\text{H}_2\text{SO}_4$  for the as-quenched steels is shown in Fig. 7, where it can be seen that in all cases, data describe two depressed, capacitive-like semicircles. The semicircle at high frequencies is related to the double electrochemical layer, whereas the second, lower frequency semicircle is related to the film formed by the corrosion products. Thus, this figure indicates that the corrosion process, in this case, is under a mixed control: charge transfer from the metal to the environment through the double electrochemical layer, and diffusion of aggressive species through the corrosion products layer. The diameter of the high frequency semicircle corresponds to the charge transfer resistance,  $R_{\text{ct}}$ , whereas the diameter of the second, lower frequency semicircle corresponds to the film resistance,  $R_{\text{f}}$ . The sum of both resistance values corresponds to the polarization resistance,  $R_{\text{p}}$ , inversely proportional to the corrosion current density value,  $I_{\text{corr}}$ . The

observed small diameter values correspond to high corrosion rate values, as observed in both Fig. 1 and Fig. 6.

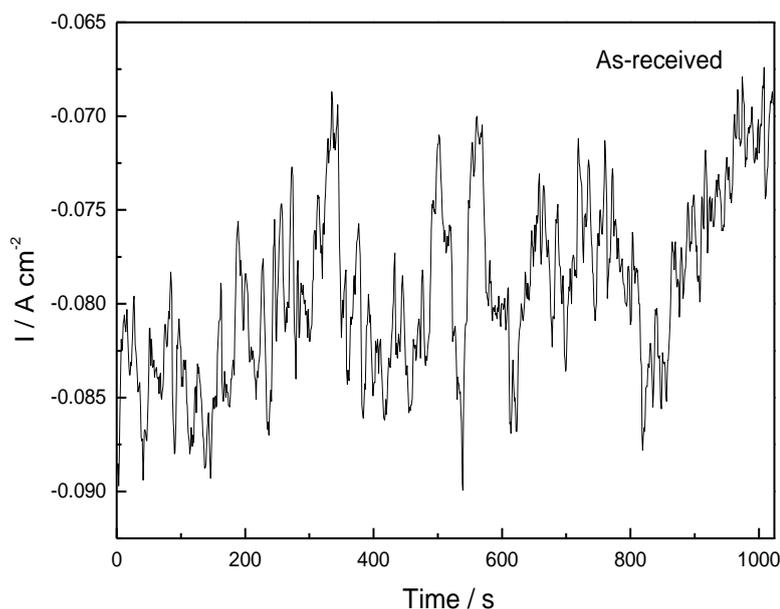


**Figure 8.** Effect of the cooling media on the Nyquist diagrams in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 60 °C, for the dual phase steel annealed at 260°C.



**Figure 9.** Effect of the cooling media on the Nyquist diagrams in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 60 °C, for the dual phase steel annealed at 400°C.

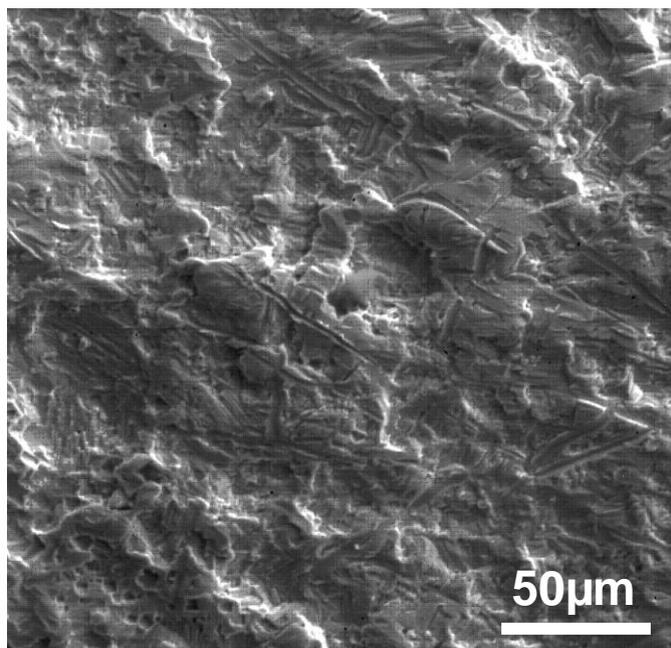
For specimens annealed either at 260 or 400°C, Figs. 8-9, the Nyquist diagrams were similar to the as-quenched specimens: two semicircles, one at high frequency values, corresponding to the double electrochemical layer, and a second semicircle at intermediate and lower frequencies, related to the corrosion products layer. The highest impedance values, thus the lowest corrosion rates, were observed for specimens annealed at 260°C, Fig. 8, just as indicated in Fig. 1 and Fig. 6. The total impedance values decreased once again with a further increase in the annealing temperature, Fig. 9. Thus, the corrosion mechanism for this dual phase steel corroded in 0.5 M H<sub>2</sub>SO<sub>4</sub> was not affected neither by the cooling media nor the annealing temperature.



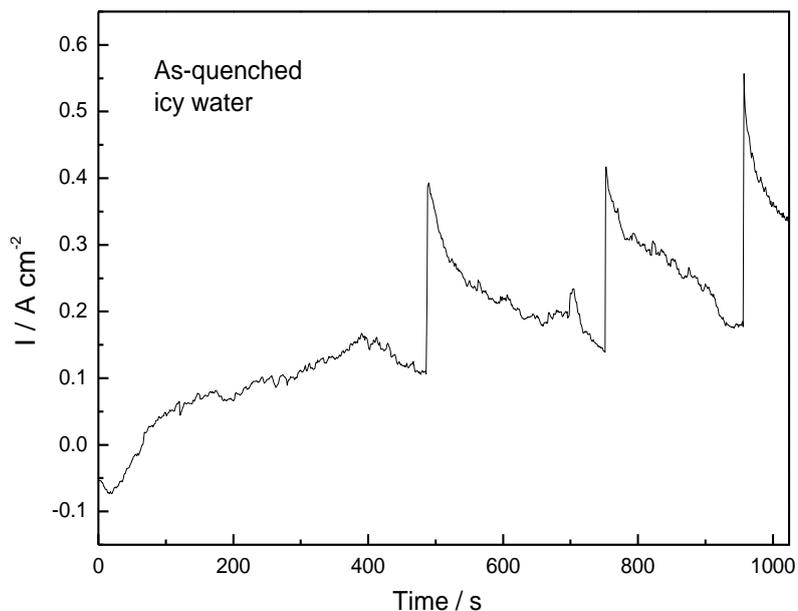
**Figure 10.** Noise in current for specimen in the as-received condition in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 60

To have an insight about the type of corrosion that this steel is susceptible to, either localized or uniform, some electrochemical noise experiments in current were performed using two identical electrodes. As an example of this, the noise in current readings for the as-received specimen is shown on Fig. 10, where it can be seen only transients of low intensity and high frequency, which corresponds to a uniform type of corrosion, as shown on micrograph of Fig. 11. All the transients are similar in intensity, without any abrupt increase, and more or less high frequency. On the other hand, the as-quenched specimen in icy water, Fig. 12, showed combination of two type of transients: one type of transients of very small intensity or amplitude but very small frequency, and a second of transients of much higher intensity with a small recovery in their original value, and very low frequency, corresponding to a type of pitting, localized type of corrosion, just as shown on Fig. 13. The small intensity, high frequency transients correspond to the low corrosion rate when the steel is covered by the corrosion products film, but when this film is disrupted, the underlying metal is not protected during a few seconds, and a localized type of corrosion such as pitting takes place, giving as a result an increase in the anodic current density value [26-28]. Once this film is re-established, the metal is

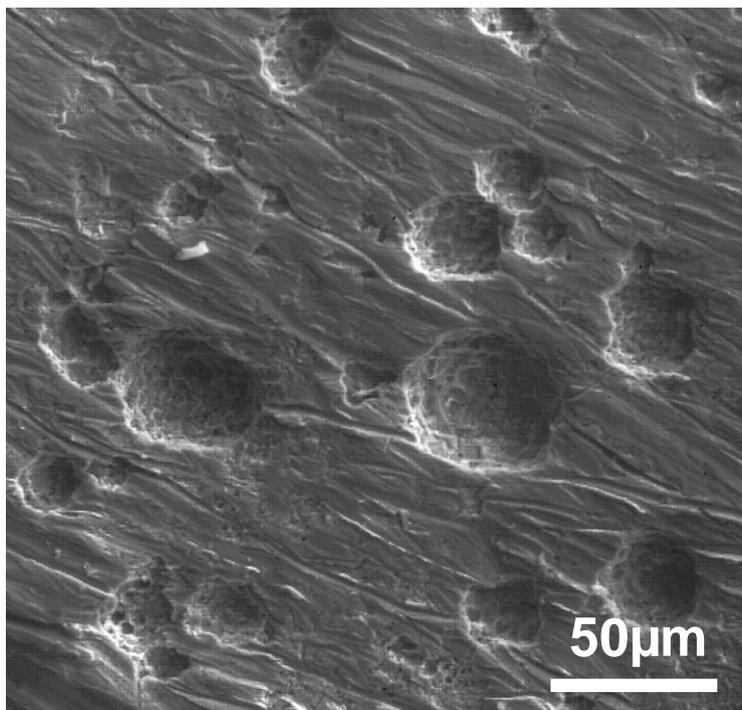
protected once again, and the anodic current is decreased, however, this film is unstable when is re-forming, and this gives as a result smaller transients in current when the overall current is decreasing.



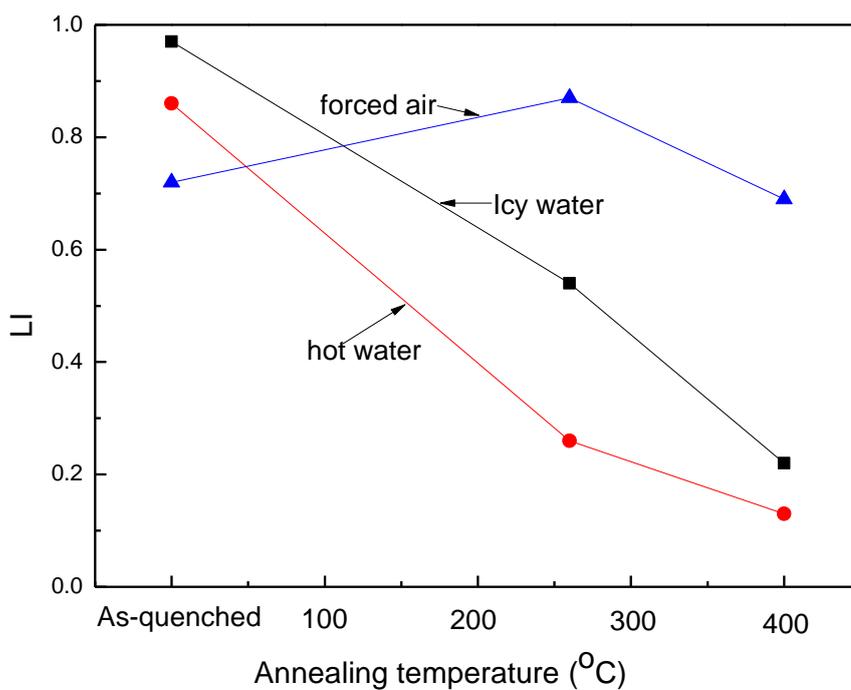
**Figure 11.** Micrograph of specimen in the as-received condition after the electrochemical noise readings in 0.5 M H<sub>2</sub>SO<sub>4</sub>



**Figure 12.** Noise in current for specimen in the as-quenched condition in icy water in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 60 °C.



**Figure 13.** Micrograph of specimen in the as-quenched condition in icy water after the electrochemical noise readings in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



**Figure 14.** Effect of the annealing temperature on the localization index value, LI, for the dual phase steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 60 °C, cooled in different media.

There is a factor called the “localization index, LI” defined as:

$$LI = \frac{\sigma_i}{i_{rms}} \quad (1)$$

where  $\sigma_i$  is the current noise standard deviation and  $i_{rms}$  is the current root mean square [29]. This shows that when the values for LI lie between 1 and 0.1, the alloy is highly susceptible to localized corrosion, when the values for LI lie between 0.1 and 0.01 the alloy is susceptible to a mixture of both uniform and localized corrosion. Finally, when the values for LI lie between 0.01 and 0.001, there is a tendency towards uniform corrosion.

Fig. 14 gives a summary of the effect of cooling media and annealing temperature on the localization index value, LI, for the dual phase steel corroded in 0.5 M H<sub>2</sub>SO<sub>4</sub>. This figure shows that all specimens in the as-quenched condition, regardless of the cooling media, have a high probability to suffer from pitting, localized type of corrosion. Generally speaking, the probability to suffer from localized type of corrosion decreases as the annealing temperature increases; however, this is not necessarily true for specimens cooled in forced air, which exhibited a high tendency towards localized corrosion regardless of the annealing temperature.

#### 4. CONCLUSIONS

A study on the effect of heat treatment on the corrosion resistance of dual phase steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 60°C has been carried out. In general terms, the corrosion rate of this steel decreases with an increase in the volume fraction of martensite. For the as-quenched specimens, the steel quenched in icy water had the highest corrosion rate, whereas quenching in hot water decreased the degradation rate. However, when annealing the steel, specimens quenched in icy water showed the lowest corrosion rate and the specimen quenched in hot water exhibited the highest degradation rate. In all cases, regardless the cooling media or the annealing temperature, the corrosion process was under charge transfer and diffusion of aggressive species through the corrosion products layer. For the specimens quenched in water, the susceptibility to localized type of corrosion decreased by increasing in the annealing temperature. The steel cooled with forced air was always susceptible to localized type of corrosion regardless of the heat treatment.

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