Correlation between Corrosion Potential and Pitting Potential for AISI 304L Austenitic Stainless Steel in 3.5% NaCl Aqueous Solution

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We investigated the effect of surface finish of two AISI 304L (UNS S30403) stainless steels on the corrosion potential (E_{corr}) in 3.5% NaCl aqueous solution and its value was compared with the pitting potential (E_p) value and the type of anodic potentiodynamic curve obtained for determination of E_p in this solution. Five different surface finishes were examined. E_{corr} and its standard deviation are strongly affected by the type of surface finish. Moreover, there are evidences of a linear correlation between E_{corr} and E_p, as well as between the percentage of anodic curves with a well-defined pitting potential and the uncertainty in the determination of E_{corr}.

1. Introduction

Passive metals may become susceptible to pitting corrosion when exposed to solutions having a critical content of aggressive ions such as ion chloride. This type of corrosion is potential-dependent and its occurrence is observed only above the *pitting potential*, E_p, which can be used to differentiate the resistance to pitting corrosion of different metal/electrolyte systems[1]. The E_p value can be determined electrochemically using both potentiostatic or potentiodynamic techniques[1].

In the potentiodynamic technique an anodic polarization curve is obtained using a constant potential scanning rate. The E_p value is the potential at which a sudden increase in the current is observed. However, for a given metal (considered as having a given chemical composition and a given microstructure) the E_p value obtained by this technique depends on the following testing variables: the potential scanning rate[2-6], the surface finish of the sample[7-12], the aeration conditions of the electrolyte[13], the immersion time prior to the test[6,8], and the geometry of the sample[14]. Moreover, the obtained anodic curve does not always yield a precise measurement of E_p. Very often, instead of a sudden increase in current density at pitting potential (normal curve - type N), this increase is slow and E_p is not well defined (curve with not defined E_p - type NDP).

In a previous work[8] it was found that the incidence of type NDP curves is strongly affected by surface finish. It was also observed[15] that the surface finish has a significant effect upon the *corrosion potential, E_{corr}*, of the metal in the testing solution, suggesting that there could be a correlation between this potential and the pitting potential. Similar observation was made by Compère *et al.*[16] who found that on average both the corrosion potential (open-circuit potential) and the pitting potential of 316L (UNS S31603) stainless steel increase with the immersion time in sea water. Moreover, they also found that a corrosion potential of around 0 mV (SCE) to 65 mV (SCE) plays a significant role in enhancing pitting corrosion resistance due to a modification of the passive film with an enrichment in chromium in the inner layer.

In present work the influence of surface finish on the corrosion potential E_{corr} of two austenitic stainless steels in 3.5% NaCl solution was investigated. The obtained values of E_{corr} are analyzed taking into account the type of the resulting anodic polarization curve for E_p determination, as well as the E_p value.

2. Experimental

The chemical composition of the two austenitic stainless steels is presented in Table 1, along with the standard

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Table 1. Chemical composition of steels.

Element (weight %)	Steel		Standard composition of AISI 304L[17]
	304L	304LL	
C	0.014	0.010	0.03 max
P	0.035	0.003	0.045 max
S	0.021	0.004	0.030 max
Mo	0.30	-	-
Cr	18.6	18.5	18.0-20.0
Ni	10.30	15.0	8.0-12.0
Si	0.45	< 0.01	1.00 max
Mn	1.76	< 0.01	2.00 max
N	0.032	0.0202	-
Cu	0.21	-	-

composition of AISI 304L (UNS S30403) steel[17]. It can be observed that the Ni content of 304LL steel is considerably in excess of the maximum value specified for AISI 304L steel. On the other hand, the C, P, S, Si, Mn and N contents in 304LL steel are lower than in 304L steel and the second "L" is used to indicate this condition.

All samples were submitted to solubilizing anneal at 1050 °C for 40 min, quenched in water, pickled with 25% HNO_3 + 8% HF at 60 °C, ground with silicon carbide paper up to the grade 600, and passivated in 20% HNO_3 solution at 35 °C for 60 min. Afterwards they were mounted in thermosetting plastic. The samples were passivated to avoid crevice corrosion at the thermosetting plastic/metal interface during the electrochemical tests. The tests were performed in a 3.5% NaCl naturally aerated solution, prepared with analytical grade reagent and distilled water, at (23 ± 1) °C.

The electrochemical tests were performed with a Princeton Applied Research potentiostat, model PAR 273, using the saturated calomel electrode (SCE) as the reference electrode and a graphite rod as the counter electrode. The pitting potential was determined by the potentiodynamic technique using a scanning rate of 1 mV/s. The scanning was always initiated after 5 min immersion time, starting from corrosion potential and finishing when the current density was at least 5000 $\mu A/cm^2$.

The corrosion potential was measured at the moment the scanning was initiated, that is, after 5 min immersion in testing solution. For some surface finishes the corrosion potential was also recorded as a function of time for a period of 96 h.

Five different surface finishes were used, namely:

S1: grade 600 silicon carbide paper grinding immediately before the immersion in testing solution;

S2: grade 600 silicon carbide paper grinding followed by an immersion in distilled and deionized water for 88 h;

S3: grade 600 silicon carbide paper grinding followed by an exposure to air in a desiccator for 88 h;

S4: grade 600 silicon carbide paper grinding followed by pickling in 30% H_2SO_4, at 35 °C for 30 min, water rinsing and drying;

S5: grade 600 silicon carbide paper grinding followed by passivation in 20% HNO_3, at 35 °C for 60 min, water rinsing and drying.

3. Results

In Figs. 1 and 2 the values of E_{corr} obtained after 5 min immersion in 3.5% NaCl solution for the different surface finishes are shown with the corresponding E_p values for 304L and 304LL steels, respectively. Both E_{corr} and E_p values are averages of at least five and up to 20 measurements, and the error bars are their standard deviations.

The data in these figures indicate that when a given surface finish determines an increase or decrease in the pitting potential value, the corresponding corrosion potential value is also increased or decreased. This can be visualized in Fig. 3, where E_p is plotted against E_{corr}. The solid lines are the result of a linear fit to the data, excluding the S2 samples because their E_{corr} does not follow the same trend as E_p. The correlation coefficients r^2 obtained are 0.88 for the 304L steel and 0.95 for the 304LL steel. The t distribution significance test shows that the probability of a linear correlation between E_p and E_{corr} is 95% for 304L steel and 97.5% for 304LL steel.
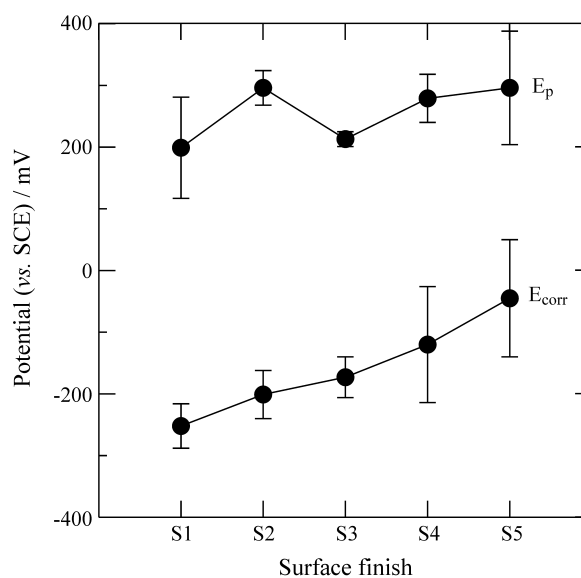

Figure 1. Pitting potential E_p and corrosion potential E_{corr} as a function of the surface finish for 304L steel.
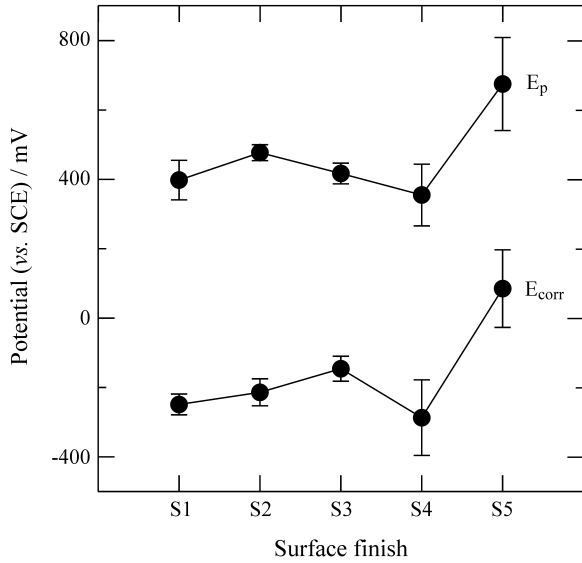
Figure 2. Pitting potential E_p and corrosion potential E_{corr} as a function of the surface finish for 304LL steel.
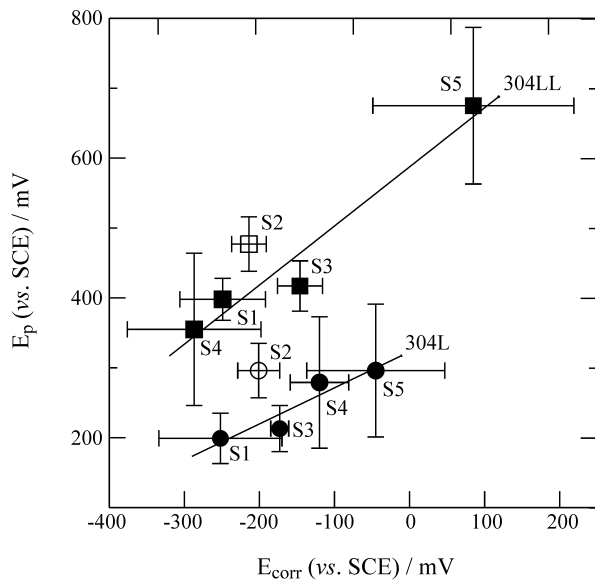

Figure 3. Correlation between pitting potential E_p and corrosion potential E_{corr} for 304L and 304LL steels.

A correlation was also observed between the percentage of type N curves obtained and the standard deviation of the corresponding corrosion potential. This correlation is presented in Fig. 4, which shows that when the standard deviation of E_{corr} is low the probability of getting a type N curve, *i.e.*, with a well defined pitting potential, is high. The correlation coefficient r^2 for this relationship is equal to 0.8127. Using the test of significance for this correlation, it was found that for a probability of 95% the confidence interval for r is 0.68 to 0.98, which assures that there is a reasonable correlation between these two variables.
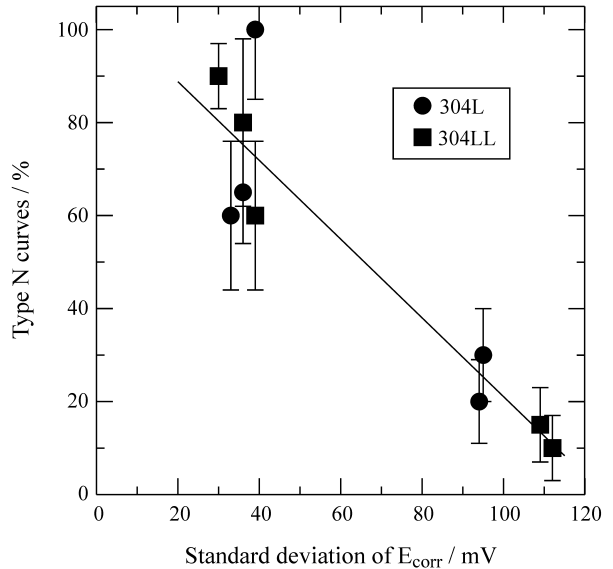

Figure 4. Percentage of obtained type N curves [data from Ref. (8)] as a function of corrosion potential E_{corr} standard deviation.

In order to get information on how E_{corr} varies with time, its value was recorded during 96 h for S1, S3, S4 and S5 surface finishes. Typical records are given on Figs. 5 to 10.

For the 304L steel with S1 surface finish the E_{corr} increases with time as shown in Fig. 5, until a value at which this potential stabilizes. 304LL steel behaves in a similar manner. The time to reach the stabilized value varies from 8 to 36 h.

For the S3 surface finish the initial value of E_{corr} is considerably high but, as shown in Fig. 6 for 304LL steel, it decreases fast until a minimum value is reached, and then
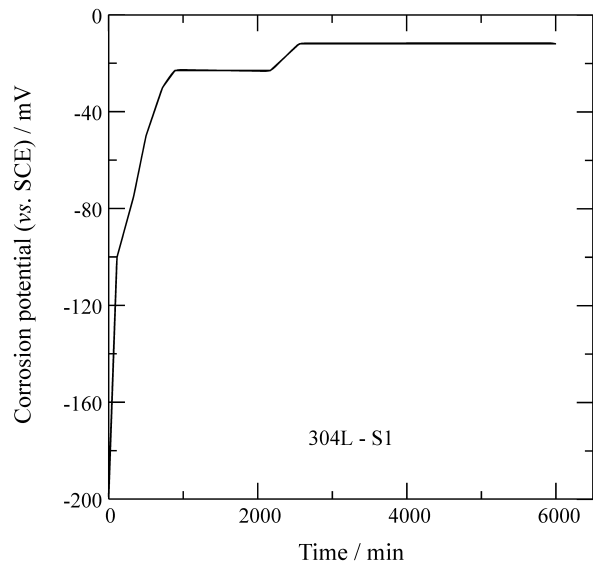

Figure 5. Corrosion potential E_{corr} variation with immersion time in 3.5% NaCl solution for 304L steel with S1 surface finish.
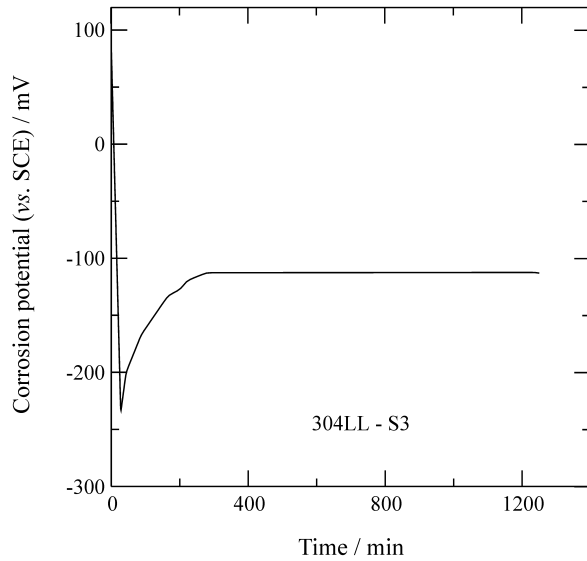
Figure 6. Corrosion potential E_{corr} variation with immersion time in 3.5% NaCl solution for 304LL steel with S3 surface finish.

Figure 7. Corrosion potential E_{corr} variation with immersion time in 3.5% NaCl solution for 304L steel with S4 surface finish.

Figure 8. Corrosion potential E_{corr} variation with immersion time in 3.5% NaCl solution for 304LL steel with S4 surface finish.
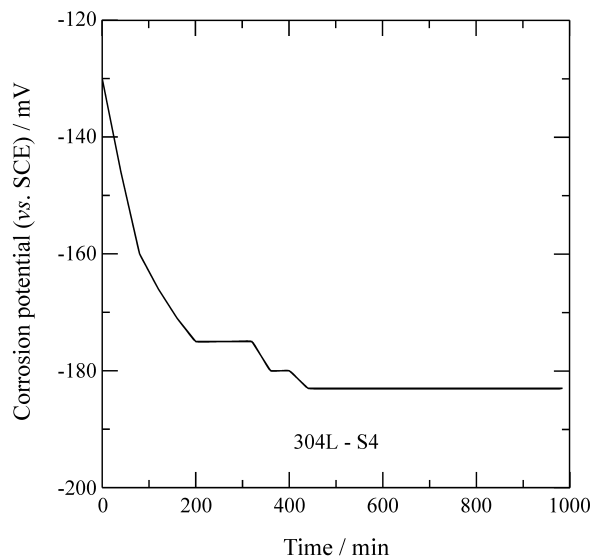

Figure 9. Corrosion potential E_{corr} variation with immersion time in 3.5% NaCl solution for 304L steel with S5 surface finish.

it starts to increase until a stabilized value is reached. 304L steel behaves in a similar manner.

The S4 and S5 surface finishes display different behaviors, which can be summarized as follows:

S4 surface finish, steel 304L: E_{corr} decreases continuously with time until a stabilized value is reached (Fig. 7);

S4 surface finish, steel 304LL: E_{corr} initially oscillates and then decreases until a stabilized value is reached (Fig. 8);

S5 surface finish, steel 304L: E_{corr} increases fast, reaches a maximum and then slowly decreases (Fig. 9);
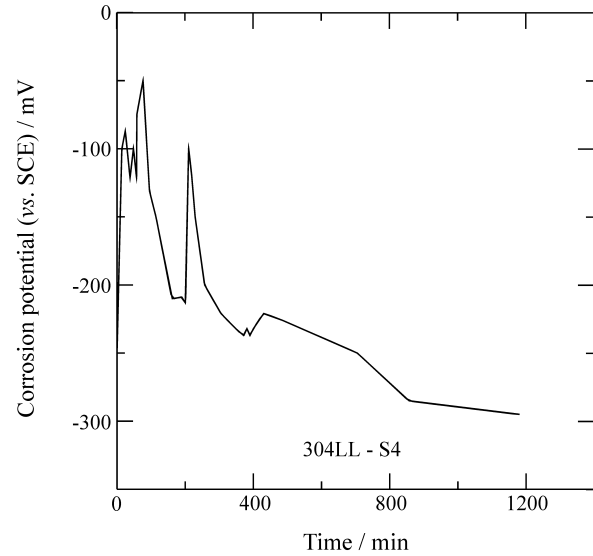
S5 surface finish, steel 304LL: its behavior, shown in Fig. 10, is similar to that of steel 304LL with S4 surface finish, shown in Fig. 8.

4. Discussion

4.1. Correlation between E_p and E_{corr}

The linear correlation observed between E_p and E_{corr} (see Fig. 3) suggests that both potentials are affected in a similar way by the quality of the passive film formed on the surface of the investigated metals by the different surface finishes, with the exception of the S2 finish. This means that for a given stainless steel in addition to E_p the E_{corr}
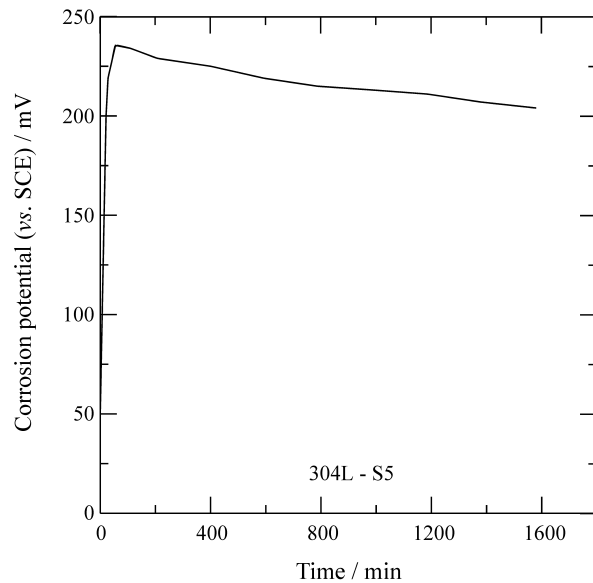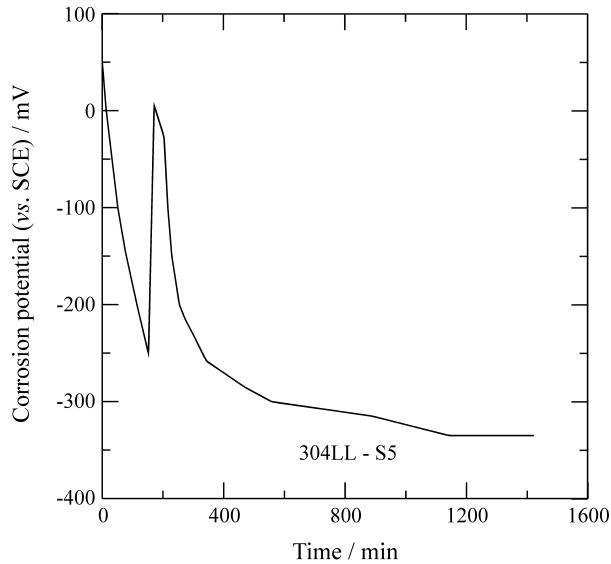
Figure 10. Corrosion potential E_{corr} variation with immersion time in 3.5% NaCl solution for 304LL steel with S5 surface finish.

value can also be used to evaluate its resistance to pitting corrosion.

The corrosion potential of a stainless steel in a neutral aerated solution, such as 3.5% NaCl, is defined by the point of intersection P of the passive range of steel anodic curve i_a with the active range of oxygen reduction reaction ($O_2 + 2H_2O + 4e \rightarrow 4OH^-$) curve i_c, as shown in Fig. 11. Thus, one or a combination of two or all of the following changes can lead to the increase of corrosion potential:

decrease of the passivation current density i_{pp}, which means the formation of a more protective passive film;
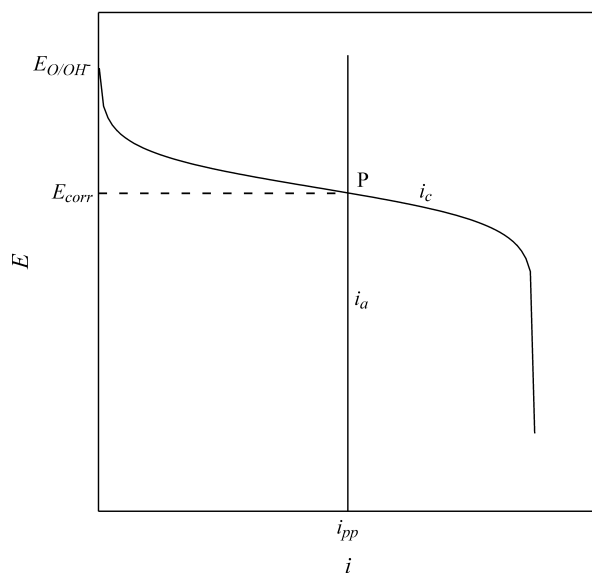

Figure 11. Corrosion potential of a stainless steel in a neutral aerated solution, defined by the point of intersection P of curves i_a and i_c.

depolarization of the cathodic curve, *i.e.*, increase of the oxygen reduction reaction exchange current density;

decrease of the Tafel slope b_c of the cathodic curve.

The first alternative, *i.e.*, the formation of a more protective passive film, seems to be the most adequate to explain the observed correlation between E_p and E_{corr}. In fact, under these conditions the breakdown of the film and the consequent nucleation and growth of a pit becomes more difficult, so that a higher pitting potential will be required to perform this breakdown. Thus, the formation of a more protective film increases at the same time both potentials, the first by making more difficult the breakdown of the film, and the second by decreasing the i_{pp} value.

It is reasonable to assume that the passive film formed under the S1 surface finish treatment is the less protective, as it is almost immediately submitted to testing after grade 600 silicon carbide paper grinding. The passive film formed under the S3 surface finish treatment is more protective because the steel samples were exposed to air during 88 h before testing, and during this time they probably developed a thicker film[18]. The same reasoning can be applied to the S2 surface finish, although it is quite possible that the nature of passive film formed under exposure to distilled and deionized water for 88 h is different because it looks more resistant to pitting than the others.

The formation of a more protective film under S5 surface finish treatment was expected, as it is well known the passivating effect the nitric acid has upon stainless steels[19]. The effect of S4 surface finish treatment, on the other hand, is puzzling, as for 304L steel the corrosion potential was only lower than that of S5, and for 304LL it was the lowest of all, the same occurring with the corresponding pitting potentials. It can be argued that for 304L steel the removal by sulfuric acid of undesirable surface inclusions should lead to a cleaner surface and, consequently, to a more uniform and protective passive film. The 304LL steel is practically inclusions free and there is no plausible reason to account for the formation of a less protective passive film after its pickling in sulfuric acid. It is proposed here that the higher Ni content in the steel would induce during pickling a certain amount of selective surface dissolution of chromium, leaving on the surface tiny chromium depleted areas, on which a poor quality film would develop. Since chromium is less noble than the other components (Fe and Ni) of the steel, this selective dissolution could be compared in some way to that of brass dezincification. This is also consistent with the findings of Yau and Streicher[20], who observed that the corrosion rate of Fe-Cr alloys in boiling 1.0 N H_2SO_4 increases with chromium content.

The second alternative implies that, in order to have a depolarizing effect upon the cathodic curve, its exchange

current density should increase. It can be shown that for the oxygen reduction reaction this happens when the pH is increased[15]. According to Skorchelletti[21], in aqueous solutions an adsorption of different species on passive films occurs, and in particular that of OH⁻ anions. In this way there could be a possibility of having a pH increase near the metallic surface, which would account for an increase in exchange current density value.

The third alternative, related with the decrease of the Tafel slope b_c of the cathodic curve, is also dependent on pH increase. Skorchelletti[21] proposes two mechanisms with several steps for reaction $O_2 + 2H_2O + 4e \rightarrow 4OH^-$, showing that in acid, neutral and slightly alkaline solutions $b_c = -118$ mV, while in alkaline solutions $b_c = -39$ mV. In this way a pH increase close to the metallic surface, caused by OH⁻ adsorption, could eventually alter the b_c value from -118 mV to -39 mV.

Even if a surface alkalization due to OH⁻ adsorption is possible, it is very difficult to explain how different surface finishes affect the amount of OH⁻ adsorbed and, consequently, the degree of surface alkalization. Thus, the second and the third alternatives seem to be very unlikely to be credited for the observed changes in corrosion and pitting potentials.

The distinctive behavior of S2 surface finish, concerning its pitting potential, seems to be associated with the formation of a passive film in water, which probably replaced the original oxide film formed in air. As will be discussed later, this situation is typically illustrated by Fig. 6, in which the oxide film formed in air suffers reductive dissolution and then is replaced by a film formed inside the solution. Apparently this new film is more resistant to pitting than the film formed in air.

4.2. Correlation between percentage of type N curves and standard deviation of E_{corr}

The linear correlation observed in Fig. 4, between the percentage of obtained N type curves and the standard deviation of corrosion potential, seems to be associated with the availability of active sites on the surface for breakdown of the passive film for pitting nucleation. As was already mentioned, the pickling with sulfuric acid of 304 L steel removes undesirable surface inclusions, leading to a cleaner surface. The same applies to the passivation treatment with nitric acid[19]. In this way the S4 and S5 finishes can be considered as leaving, on the surface of 304L steel, less active sites than the other finishes.

If the number of active sites is small, a condition can be reached where, for instance, the breakdown of passive film becomes essentially a probabilistic phenomenon. This means that in a given test this breakdown would be fast while in another test it would be considerably slow, causing

therefore a large dispersion in experimental results. This assumption is the same of the stochastic approach proposed by several authors[22-26] to explain the large dispersion in pitting potential measurements.

The reason for the large dispersion of the corrosion potential for 304LL steel submitted to the S4 and S5 surface finishes seems to be different. As can be observed in Figs. 8 and 10 its corrosion potential variation with time is very complex. This complexity could be a consequence of the proposed selected surface dissolution of chromium, which could occur also during the passivation treatment in nitric acid. The observed potential oscillation is then a good reason for the large standard deviation.

The same reasoning used to explain the large standard deviation of the 304L steel corrosion potential applies also to the small percentage of the type N curves. The nucleation of a pit requires an active site and if the number of these sites is small the process becomes stochastic. For 304LL steel, however, there is not a clear idea on how the proposed selective dissolution of chromium affects the pitting process.

4.3. Variation of E_{corr} with time

The long term tests of E_{corr} variation with time, given in Figs. 5 through 10, pointed out the complexity of processes involving the immersion of stainless steel inside an aqueous solution. Probably the best understood behavior is that displayed by steels submitted to the S3 surface finish treatment, shown in Fig. 6. This behavior, reported in literature[27], is typical of the reductive dissolution of an oxide film formed in the air, followed by the growth of a new film inside the solution. The reductive dissolution requires the breakdown of the film so as to allowing metal dissolution to occur, such as:

$$Fe \rightarrow Fe^{2+} + 2e \tag{1}$$

and that of the other components of the alloy (Cr and Ni).

This reaction provides the necessary electrons for the cathodic dissolution of oxide:

$$Cr_2O_3 + 6H^+ + 2e \rightarrow 2Cr^{2+} + 3H_2O \tag{2}$$
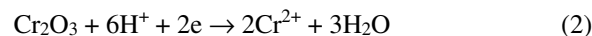
As indicated in Fig. 6, the oxide dissolution process is dominant during the initial stage of the test, when the corrosion potential decreases rapidly with time until a minimum is reached. After this, the growth of the new film inside the solution takes over.

It is quite possible that steels submitted to the S1 surface finish treatment also behave in a similar way. Although there are no signs, as shown in Fig. 5, of dissolution taking place, it must be remembered that in this case the steels were immediately immersed inside the solution after grinding, so that the amount of oxide film formed in air was

probably insignificant. This type of behavior is analogous to that reported by Fenili and Wolynec[18], in which the time between the surface grinding of an AISI 304 steel sample and its immersion inside a nitric acid solution had a significant effect upon the time for the dissolution to start. When the sample is immediately immersed, the dissolution takes place in a few seconds; on the other hand, if the sample is immersed in the following day, the dissolution only starts after about 10 min.

The behavior of the 304L steel submitted to the S4 surface finish treatment, shown in Fig. 7, suggests a reductive dissolution, but there is no indication of new film growth. Moreover, the corrosion potential decrease is neither very fast nor large (just about 50 mV). Thus, it seems more likely that the passive film remains on the surface of the metal and that the potential decrease is caused by specific adsorption of Cl$^-$ ions, which would render the passive film less protective.

For the 304L steel treated in nitric acid (S5), the curve shown in Fig. 9 indicates that the film formed in this acid is very stable. No dissolution is detected in the initial stage, on the contrary, the increase in the corrosion potential suggests that this film continues to grow inside the testing solution, until a maximum is attained. After that the corrosion potential decreases slowly and this could imply in a slow dissolution.

Remarks have already been made on the complex behavior, shown in Figs. 8 and 10, of 304LL steel treated in sulfuric (S4) and nitric acid (S5). It can be added here that the observed oscillatory behavior is consistent with the proposed mechanism of selected dissolution of chromium. Actually, when a chromium depleted area is taken away by corrosion, a surface with normal chromium content is exposed to the solution and a new passive film is formed on it. When this happens, the corrosion potential increases. This process is repeated until the removal of chromium depleted areas is completed. It is not clear why the final corrosion potential is so low (about -300 mV, SCE).

5. Conclusions

The corrosion potential E_{corr} of 304L and 304LL stainless steels in 3.5% NaCl aerated solution, as well as its standard deviation, are strongly affected by the type of surface finish.

A linear correlation between the pitting potential E_p and the corrosion potential E_{corr} was observed for four of the five surface finishes tested. For the S2 surface finish, in which the sample was immersed in distilled and deionized water for 88 h before being submitted to testing, the difference between these potentials is considerably larger than that anticipated by the above linear correlation.

A reasonable negative linear correlation was also observed between the percentage of curves obtained with a well defined E_p (type N curves) and the standard deviation of E_{corr}. The larger standard deviations were obtained for samples submitted to pickling in sulfuric acid (S4 surface finish) and to passivation treatment in nitric acid (S5 surface finish).

The above correlations imply that the E_{corr} value can also be used to evaluate the resistance of a given stainless steel to pitting corrosion.

For samples submitted to S1 (immediate immersion inside the testing solution) and S3 (exposure of the sample to air for 88 h) surface finish treatments, the E_{corr} dependence with time, observed in the longer duration tests in 3.5% NaCl solution, seems to be caused by the reductive dissolution of the oxide film formed in the air, followed by the growth of a new film inside the testing solution. For S4 and S5 surface finishes the behavior is considerably complex, in particular for the 304LL steel, requiring further investigation for its understanding.

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