ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY CHARACTERIZATION OF THE FILMS DEVELOPED ON STAINLESS STEELS

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The electrochemical behaviour of films formed on AISI 316 and AISI 304L by cyclic voltammetry in alkaline medium is studied by EIS. Impedance spectra were obtained each 100mV from –1.057V to 0.443V (vs.Hg/HgO), in order to scan the different activity regions detected in voltammetric studies, i.e.: iron activity, passivity and Cr-Ni-Mo activity zones (Fig. 1).

The chemical composition of the passive films has been studied by X-ray photoelectron spectroscopy (XPS). EIS and XPS have proved to be very sensitive in the characterisation of the passive films generated.

After eight voltammetric cycles in NaOH 0.1 M, the impedance spectra recorded all over the scanned potential range show three time constants for both steels. Those spectra have been fitted using a suitable equivalent circuit. The dependence of the best fitting parameters on electrode potential is similar for both alloys, but with higher resistance values for AISI 316. Nevertheless, near the transpassive region an important impedance decreasing is observed for this last alloy (Figure 2).

These results are in good agreement with the voltammetric curves: for both stainless steels the same features are detected, but the peaks assigned to iron and chromium oxidation processes are lower for the AISI 316. Only the current densities related to the Ni^{2+}/Ni^{3+} redox process are increased. Moreover it is necessary to take into account the effect of Mo in this alloy. As it can be deduced from the voltammetric curves obtained from a sample of pure molybdenum (not shown here), high current values are registered at those potentials due to the Mo^{4+}/Mo^{6+} process. So the effect of the higher content in those elements for the 316 can justify the impedance values detected.

In order to characterise the resistivity of the developed films; a more detailed analysis in the high frequency range was made on both stainless steels, after eight voltammetric cycles in NaOH 0.1M. Impedance spectra were registered at the corrosion potential between 10 MHz and 1kHz using a HP 4194A Impedance Analyser, and an electrochemical cell with two identical working electrodes. The obtained Nyquist diagrams are plotted in Figure 3, where the difference in the resistive film behaviour is shown.

The final paper will present the in depth discussion on the experimental results. XPS characterisation of the passive films will be employed to help in understanding the electrochemical data.

Acknowledgements
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References

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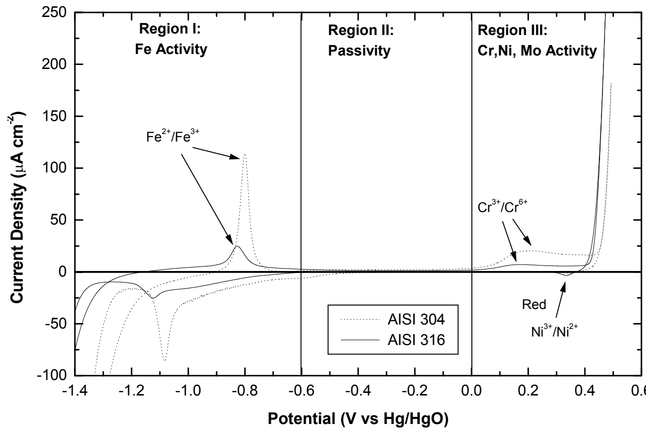

Figure 1.- Fifth voltammetric cycle for AISI 304L and 316 obtained in NaOH 0.1 M.

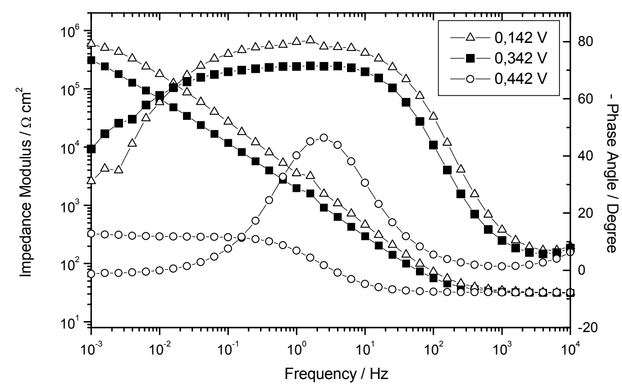

Figure 2.- Bode diagram for the AISI 316 obtained at three electrode potential values (vs. Hg/HgO), in NaOH 0.1 M after 8 voltammetric cycles.

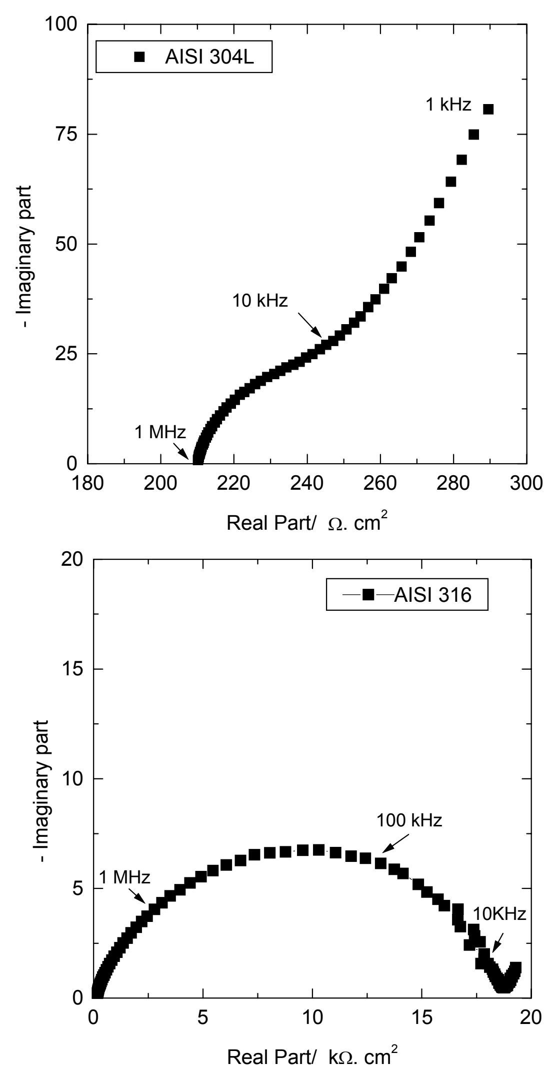

Figure 3.- Nyquist diagrams for AISI 304L and AISI 316 at the corrosion potential showing the differences in dielectrical properties.