

IMPEDANCE SPECTRA FOR ALUMINUM 7075 DURING THE EARLY STAGES OF IMMERSION IN SODIUM CHLORIDE

João C. S. Fernandes

Grupo de Estudos de Corrosão e Protecção - Dept. de Eng. Química
Instituto Superior Técnico - Av. Rovisco Pais, 1096 Lisboa Codex, Portugal

Florian Mansfeld

CEEL - Department of Materials Science and Engineering
University of Southern California - Los Angeles, CA 90089-0241, U.S.A.

ABSTRACT

The impedance spectra obtained at short exposure times for Al 7075-T6 immersed in 0.5 N NaCl do not agree with the pitting model proposed by Mansfeld and co-workers. Instead of a transmission line impedance, an inductive loop is observed at low frequencies. This result is due to the non-linearity of the system at short exposure times, when E_{CORR} is close to E_{pit} . The application of the anodic portion of the ac signal causes this non-linear behavior. The observed impedance is therefore a system response and not a true impedance. For longer exposure times agreement with the pitting model is observed.

INTRODUCTION

Extensive investigations of Al alloys and Al-based metal matrix composites (MMC) exposed to NaCl have shown that the impedance behavior changes from the simple R_p-C_p model for passive Al to a more complicated behavior which is explained by the pitting model proposed by Mansfeld and co-workers [1-3]. In the course of these investigations it was also observed that for very short exposure times (i.e. 24 h or less) the impedance spectra did not agree with the pitting model. These deviations were considered to be due to experimental artifacts or non-linearities of the systems and were therefore not investigated further in the past. We have now done a more detailed study and present our results for the very earlier stages of pitting.

RESULTS AND DISCUSSION

The impedance spectra obtained for Al 7075-T6 at E_{CORR} after 1 h of immersion in 0.5 M NaCl are shown in Fig. 1a, where an inductive loop can be seen in the Nyquist plot. In the current vs time plot obtained during this measurement a sharp current peak is observed for anodic potentials, distorting the sinusoidal wave pattern (Fig.1b). Since the current response to the applied sinusoidal potential signal is not sinusoidal, it has to be concluded that the system is non-linear [4].

The reason for this non-linear behavior can be found in the polarization curve for Al 7075-T6 in the same solution. As the pitting potential, E_{pit} , and E_{CORR} are nearly the same, even a small increase of the potential E above E_{CORR} will lead to the initiation or acceleration of pitting with a large increase of the anodic current i , whereas for cathodic potentials an almost vertical E vs i line is found with very small currents. In this case, the impedance measured around the corrosion potential will no longer be the ratio of two sinusoidal signals with the same frequency and different amplitudes and phases, but will be due to a non-sinusoidal current signal, which is considered to be the reason for the inductive behavior shown in Fig.1a.

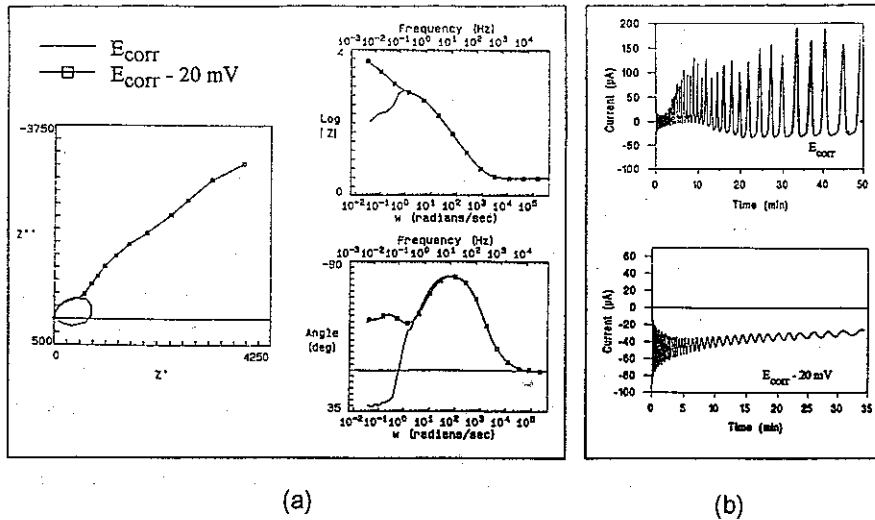


FIG.1 - Impedance spectra (a) and current vs time plot (b) at E_{CORR} and $E_{CORR} - 20 \text{ mV}$ for 1 h of immersion.

In order to avoid this non-linearity problem, impedance spectra were taken at an applied cathodic potential of -20 mV vs E_{corr} (Fig. 1a). In this case, the results agree with the pitting model proposed by Mansfeld et al [1-3] and the current vs time plot shows a sinusoidal current response (Fig. 1b). Moreover, the high-frequency region of these impedance spectra coincides with that obtained at E_{corr} .

Impedance spectra obtained after 3 days of immersion, either at E_{corr} or $E_{\text{corr}} - 20$ mV, are identical and the current vs time plots for both cases show sinusoidal wave patterns. The spectra agree with the pitting model. From these results it can be concluded that recording of EIS data at a potential which is 20 mV cathodic to E_{corr} does not affect the validity of impedance measurements aimed at analyzing the pitting behavior of Al alloys.

REFERENCES

- [1] F. Mansfeld, S. Lin, S. Kim and H. Shih, *J. Electrochem. Soc.* **137**, 78 (1990)
- [2] F. Mansfeld, *Electrochim. Acta* **35**, 1533 (1990)
- [3] F. Mansfeld, Y. Wang, H. Xiao and H. Shih, in Proc. "Critical Factors in Localized Corrosion", The Electrochem. Soc., Proc. Vol. 92-9, p. 469, 1992
- [4] F. Mansfeld and W. J. Lorenz, in "Techniques for Characterization of Electrodes and Electrochemical Processes", J. Wiley, p. 581, (1981)