SHORT COMMUNICATION

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

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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 the impedance behavior 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]. When pits have exceeded a certain minimum size [3], a transmission line impedance is observed at low frequencies. Mansfeld et al have determined pit growth rates for Al alloys exposed to NaCl from EIS-data obtained at the corrosion potential E_{corr} [2,3]. 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 early stages of pitting in the hope to avoid confusion in comparisons of our long-term EIS-data with those obtained by others, who might have collected EIS-data only for very short exposure times.

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EXPERIMENTAL APPROACH

Electrochemical impedance spectra were obtained for Al 7075-T6 in 0.5 M NaCl solution (open to air) with simultaneous recording of current vs time for frequencies below 1 Hz.   Measurements were carried out with a Solartron model 1250 Frequency Response Analyser and a Solartron model 1286 Electrochemical Interface. The current output from the potentiostat was recorded using a Linseis L4000 chart recorder. The spectra were obtained either at E_{corr} or at 20 mV negative to E_{corr} using an applied a.c. signal of 10 mV (rms). A three-electrode cell [1] was used exposing 20 cm^2 of the test electrode. All surfaces were degreased and polished up to 1200 grit prior to immersion. Polarization curves were obtained using a PAR 173 potentiostat with appropriate software.

RESULTS AND DISCUSSION

The impedance spectra obtained at E_{corr} after 1 h of immersion in NaCl are shown in Fig. 1a, where an inductive loop can be seen in the complex plane plot. In the current vs time plot obtained during this measurement sharp current peaks are 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.
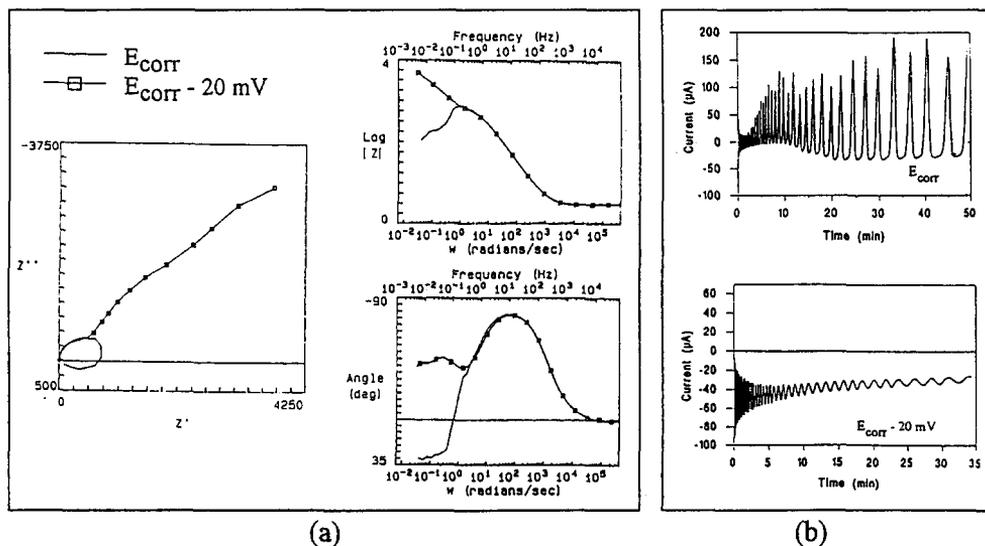

(a)   (b)

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

The reason for this non-linear behavior can be found in the polarization curve for Al 7075-T6 in the same solution (Fig. 2). 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 density i. For cathodic potentials an almost vertical E vs i line is found with very small currents. In this case, the measured impedance 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 signal, which is considered to be the reason for the inductive behavior shown in Fig.1a.
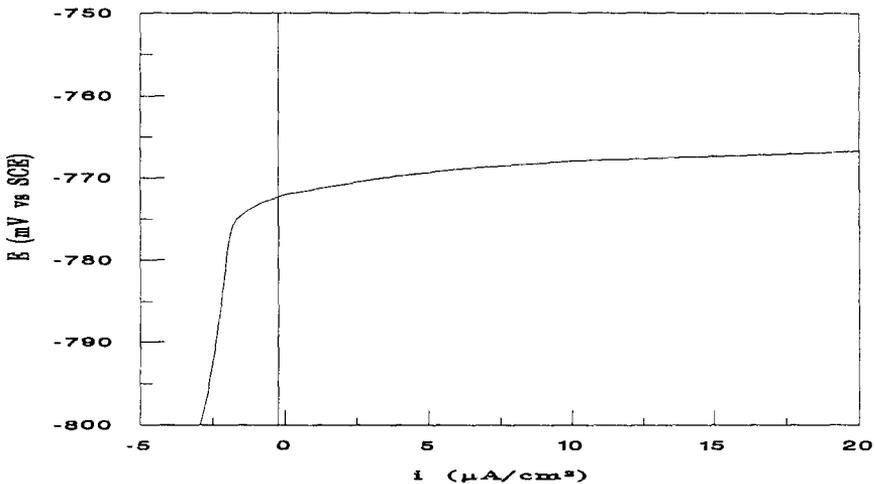

FIG.2 - Polarization curve for Al 7075 T6 in 0.5 M NaCl solution.

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, which is dominated by the electrode capacitance, coincides with that obtained at E_{corr}.

After several hours of immersion, E_{corr} tends to decrease, but E_{pit} remains constant. Impedance spectra obtained after 3 days of immersion, either at E_{corr} or E_{corr} - 20 mV, are very similar (Fig. 3a) and the current vs time plots for both cases show sinusoidal wave patterns (Fig 3b). 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 during the early stages of immersion. It has to be remembered that for the majority of the exposure time the sample is at E_{corr}. Only for the recording of the EIS data E_{corr}-20mV is used to avoid the problems discussed above.
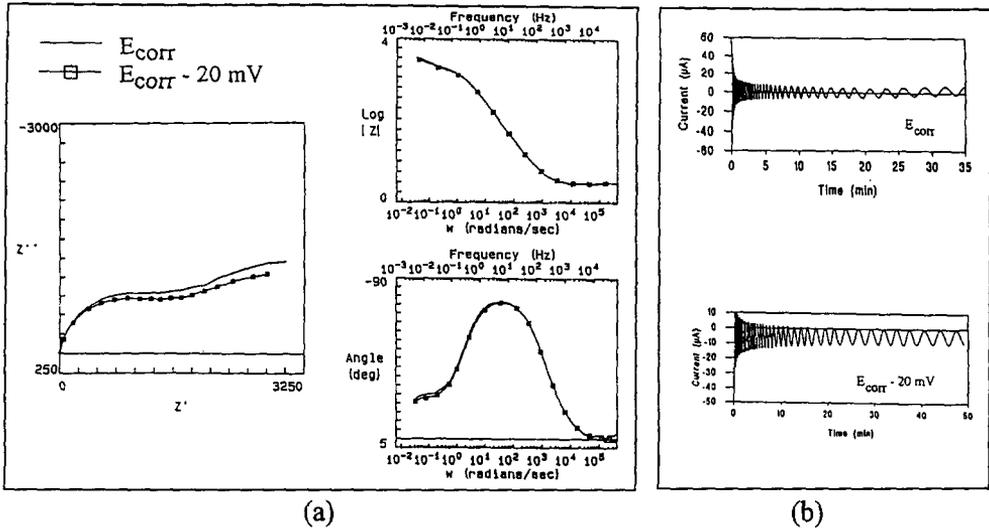
(a)   (b)

FIG.3 - Impedance spectra (a) and current vs time plot (b) at E_{corr} and E_{corr}-20 mV for 3 days of immersion.

CONCLUSIONS

In the early stages of immersion, when E_{pit} and E_{corr} are almost identical, the application of the anodic part of the applied ac signal causes initiation or acceleration of localized corrosion. The system is not linear at this time, therefore the observed impedance is a system response and not a true impedance [4]. This situation is similar to the case of propargylic alcohol as a corrosion inhibitor for iron in H_2SO_4, where the inhibitor desorbs during the anodic portion of the applied ac signal and an inductive loop appears. At longer immersion times this non-linearity problem disappeared [5].

References

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