

SHORT COMMUNICATION

Electrochemical impedance studies on pure aluminium in carbonate solution

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1. Introduction

The development of lightweight aluminium alloys with higher specific strength and stiffness and better resistance to environmental corrosion is a priority subject in advanced materials technology. Previously, work has been done on these alloys with the aim of understanding their electrochemical behaviour in different solutions [1–3]. However, for comparative purposes it is necessary to conduct electrochemical experiments on pure aluminium.

Electrochemical impedance spectroscopy has been applied successfully to various studies involving aluminium alloys, but in a wide number of cases the alloy was previously anodized and sealed under different experimental conditions [4, 5]. Correlations were found between impedance measurements and the corrosion resistance of these alloys.

In the present study, a.c. impedance measurements were also carried out in order to characterize the electrochemical interface in a 0.01 M Na₂CO₃ solution, but without any previous modification of the aluminium surface.

2. Experimental details

High purity aluminium (Al 99.999%) rod electro-machined to discs at 1 cm diameter was used. The specimens were mounted in epoxy resin and abraded to 1000 grit.

D.c. polarization measurements were carried out in unstirred deaerated aqueous 0.01 M Na₂CO₃ solution at ambient temperature. A three electrode conventional cell with graphite counterelectrodes and a saturated calomel reference electrode (SCE) was used to which all potentials are referred. The potential was supplied by a Solartron 1286 Electrochemical Interface, controlled by an HP87 microcomputer associated with an HP9121 floppy disc drive, and swept between a slightly cathodic potential (–1.850 V) and 2.0 V, at a sweep rate of 100 μV s⁻¹. Data acquisition was made simultaneously by the same system.

A.c. impedance spectra were taken at various potentials along the polarization plot on the same cell. A Solartron 1250 Frequency Response Analyser, remotely controlled by the above described computing facilities, was used.

3. Results and discussion

Figure 1 shows the polarization plot for the aluminium

in the 0.01 M Na₂CO₃ solution. When the potential is increased above the rest potential, an increase of current with potential is observed up to a maximum of 0.130 mA cm⁻² at –1.0 V. Between –1.0 V and –0.530 V, the current decreases with potential, increasing again slightly between –0.530 V and –0.1 V. Above this potential the current decreases and attains an almost constant value of approximately 0.100 mA cm⁻². This is related to the presence of a film on the surface which is visible with the naked eye.

Impedance measurements taken at –1.609 V (rest potential) are shown in Fig. 2 as a Nyquist plot. This plot consists of a semicircle followed at lower frequencies by a straight line. Analysis of the semicircle gives values of a charge transfer process ($R = 240 \Omega \text{ cm}^{-2}$, $C = 14 \mu\text{F cm}^{-2}$) that are typical of metallic dissolution. The corresponding Bode diagram, Fig. 2, illustrates the same features.

The results at the rest potential were also obtained using a rotating disc electrode at 1000 and 4000 rpm. The low frequency straight line changes considerably with the rotation speed, this being indicative of a diffusion controlled process. Moreover, as the speed of the disc increases, the thickness of the diffusion layer becomes smaller.

At –1.20 V the impedance diagram changes shape at low frequencies, Fig. 3. A capacitive-inductive loop appears followed by an almost straight vertical line, typical of pure capacitive behaviour. Spectra of identical shape were found by Schuhmann [6] for anodized aluminium in ethanol and the presence of such loops was also found by other authors [7, 8] for anodized aluminium alloys and passive iron. The Bode diagram also indicates the capacitive behaviour, showing, at low frequencies, a line with a 45° slope. At high frequencies the response continues to be characteristic of a charge transfer process of metallic dissolution ($R = 825 \Omega \text{ cm}^{-2}$, $C = 13.5 \mu\text{F cm}^{-2}$).

The loop in Fig. 3 was successfully computer simulated [9] by using an R–C network in series with the faradic resistance in a Randles-type equivalent circuit. However, the values of the R and C components had to be considered as ‘negative’ for which, although seemingly difficult to understand from an electrical point of view, they have also been found in other studies, under different experimental conditions, and have been associated with inhibition of metallic dissolution in an active-passive transition on the surfaces [10–12] and adsorbate species [13–15]. In our case both hypotheses are plausible.

At potentials of –0.850 V and 0.0 V, Fig. 4, the

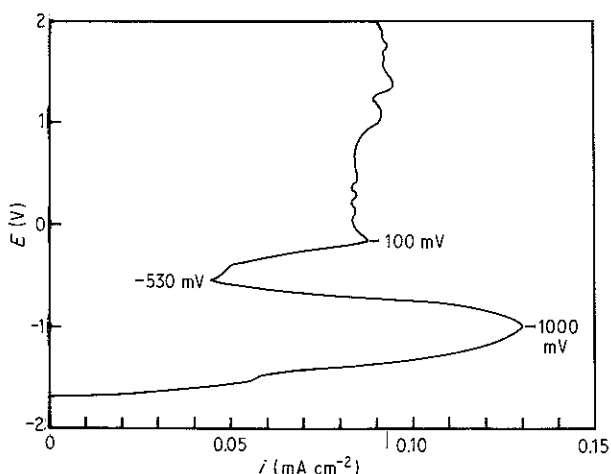


Fig. 1. D.c. polarization plot for pure aluminium in 0.01 M Na₂CO₃ solution.

shape of the impedance plots is the same as that obtained at -1.20 V. However, whereas at zero potential the value of the semicircle diameter, i.e., the charge transfer resistance, increases about two-fold compared to that at -1.20 V, for -0.85 V only a very slight increase is noticed. The value of the capacitance is constant ($C = 13.5 \mu\text{F cm}^{-2}$) for this latter case, but in the former case becomes much lower ($C = 5.1 \mu\text{F cm}^{-2}$), which is typical of a film covering the whole surface is postulated, the dissolution occurring through this film.

At lower potentials, although a film exists on the surface, it does not cover the substrate completely, Fig. 5, and the dissolution occurs at the bare metal. This situation is different from the case where an anodized film is previously formed on the aluminium. The electrochemical data also support this. In the latter case the impedance data [4, 5] reflect the presence of a porous and a barrier layer on the surface, as generally accepted for anodized films [4, 16], with the data usually fitting a transmission line model. The film is 10 to 50 μm thick. In the present study the film is much thinner and such a model is not applicable, as shown by the rotating disc results.

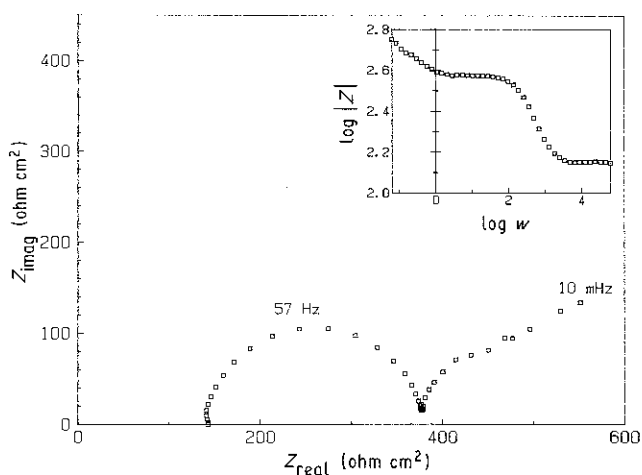


Fig. 2. A.c. impedance plot for pure aluminium in 0.01 M Na₂CO₃ solution at -1.609 V_{SCE}. Inset: Bode diagram.

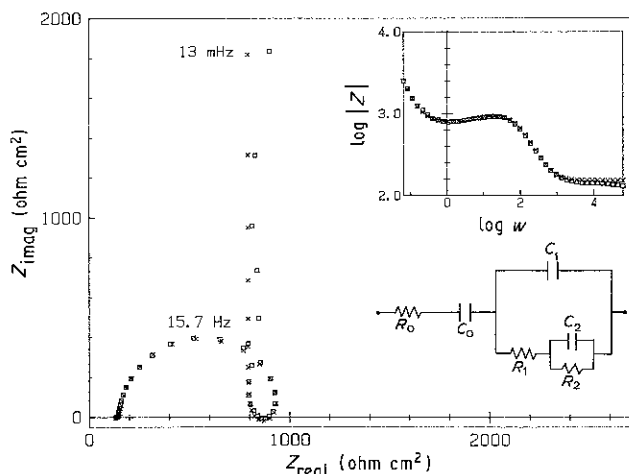


Fig. 3. A.c. impedance plot for pure aluminium in 0.01 M Na₂CO₃ at -1.20 V. \square = Experimental, \times = Simulation. ($R_0 = 152 \Omega \text{ cm}^2$, $C_0 = 6800 \mu\text{F cm}^{-2}$, $R_1 = 825 \Omega \text{ cm}^2$, $C_1 = 13.5 \mu\text{F cm}^{-2}$, $\theta = 1.9^\circ$, $R_2 = -185 \Omega \text{ cm}^2$, $C_2 = -850 \mu\text{F cm}^{-2}$.)

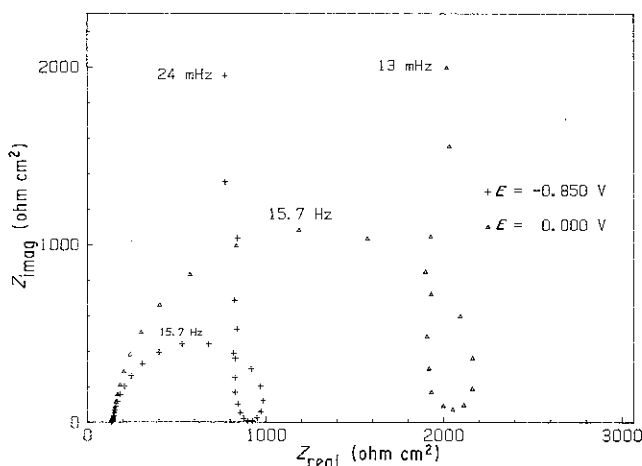


Fig. 4. A.c. impedance plots for pure aluminium in 0.01 M Na₂CO₃ solution at (+) -0.850 V and (Δ) 0.0 V.

4. Conclusions

Impedance measurements account for both the formation of a film on the metallic surface and metallic dissolution. At lower potentials the film does not completely cover the surface and diffusion controlled metallic dissolution takes place at the bare metal, whereas for higher potentials, where the d.c. current is almost stable, the a.c. response reveals a dissolution process on a surface covered with a continuous film.



Fig. 5. Scanning electron micrograph of the aluminium surface, showing the discontinuous structure of the film.

The films formed in the present case are rather different from the anodizing films where a porous structure usually fits a transmission line model for the impedance data.

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