

# Characterization of Anodically Formed Porous and Barrier Oxide Layers on Aluminium Using Electrochemical Impedance Spectroscopy

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Filmes de óxidos porosos formados através da anodização de ligas de alumínio em soluções aquosas ácidas, e selados em diferentes tempos de imersão em água destilada quente, foram estudados usando-se a espectroscopia de impedância eletroquímica (EIS). Também analisou-se as propriedades eletrônicas de camadas barreiras finas de óxido de alumínio. As características destas camadas de óxido superficial foram investigadas em função da liga de alumínio e da composição da solução. A análise dinâmica destes sistemas eletroquímicos permitiu determinar o grau de hidratação dos filmes porosos bem como as propriedades de semi-condução do tipo n das camadas barreiras de alumina.

Porous oxide films formed by anodizing of aluminium alloys in acidic aqueous solutions and sealing for different exposure times in hot distilled water were studied using electrochemical impedance spectroscopy (EIS).

Similar efforts were employed to analyze the electronic properties of thin aluminium oxide barrier layers. The characteristics of these surface oxide layers were investigated depending on aluminium alloy and solution composition. The dynamic analysis of these electrochemical systems allowed to determine the hydration degree of the porous films as well as the n-type semiconduction properties of the alumina barrier layers.

**Key words:** *anodized aluminium; alumina barrier layers; aluminium oxide; electrochemical impedance spectroscopy.*

## Introduction

Aluminium finds wide commercial applications because of the improved corrosion and abrasion resistances achieved through anodizing processes. Physicochemical and electrochemical aspects of porous/barrier oxide films obtained by anodic oxidation of aluminium and its alloys in different aqueous electrolytes, sealed using different procedures, have been extensively studied in the last decades<sup>1-8</sup>. In spite of the various contributions to analyze the kinetics of growth, composition, and structure of the

thin alumina barrier layers, their electronic properties are not well understood yet<sup>9,10</sup>. Furthermore, up to now only a few papers have dealt with the influence of the surface film hydration on the performance of sealed anodized aluminium<sup>11,12</sup>.

The present paper deals with the physicochemical characterization of anodized aluminium by electrochemical impedance spectroscopy, paying particular attention to the influence of the alloy composition, nature of the acidic electrolyte solutions employed for the anodizing, and sealing time.

## Experimental

Alloys 1050 (Al 99.95%) and Al-0.4%Mn, and high purity Al (99.996%) were used as working electrodes. The anodizations were carried out using DC conditions in the following electrolyte solutions: (A) 1 M H<sub>2</sub>SO<sub>4</sub>; (B) 1 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M H<sub>3</sub>BO<sub>3</sub>; and (C) 0.5 M H<sub>3</sub>BO<sub>3</sub> + 0.05 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.

Porous layers produced at constant formation potential and anodization time (30- $\mu$ m thickness) using solutions A and B were sealed in hot water at different immersion times. The corresponding impedance spectra were obtained in 3.5% K<sub>2</sub>SO<sub>4</sub> aqueous solution at the open circuit corrosion potential. On the other hand, the anodic alumina barrier layers produced in solution C were characterized in the same anodizing solution starting at the formation potential  $E_f = 1.79$  V and proceeded by potential steps of 0.2 V towards more negative potentials up to 0.39 V (10- $\mu$ m constant thickness).

The EIS measurements were performed covering a wide frequency range ( $0.1 \text{ Hz} \leq f \leq 50 \text{ kHz}$ ) using Solartron EI1186 and FRA 1250 integrated with a PC computer system. Complete details of the hardware arrangement and software procedures have been given elsewhere<sup>13,14</sup>. In all cases the working electrode geometric area was 1.13 cm<sup>2</sup>.

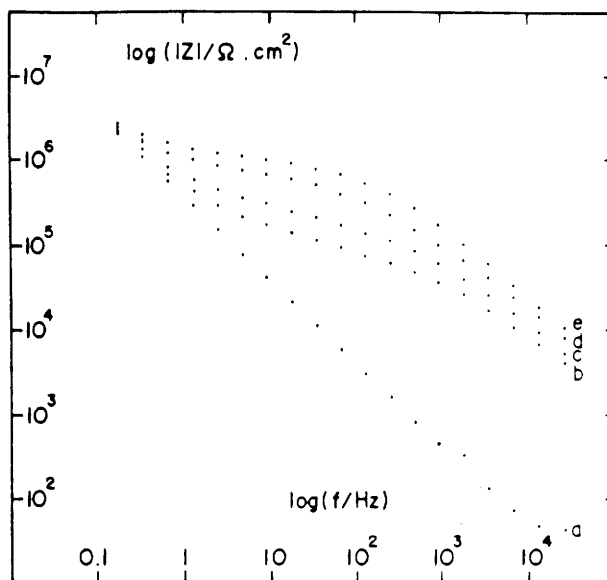
## Results And Discussion

*1. Porous oxide layers:* the passivation of aluminium is initially produced by the formation of a hydrated hydroxide film<sup>6</sup>. At the early stages of the electrochemical formation, the thin oxide film is generally amorphous and grows by ionic transport through a high electric field since alumina is an electric insulator with no free electrons in the conduction band. These thin films exhibit rectification and electroluminescence<sup>15</sup>. When thicker layers are formed they are porous, acquiring a double structure, and their poor corrosion performance can be improved by sealing procedures.

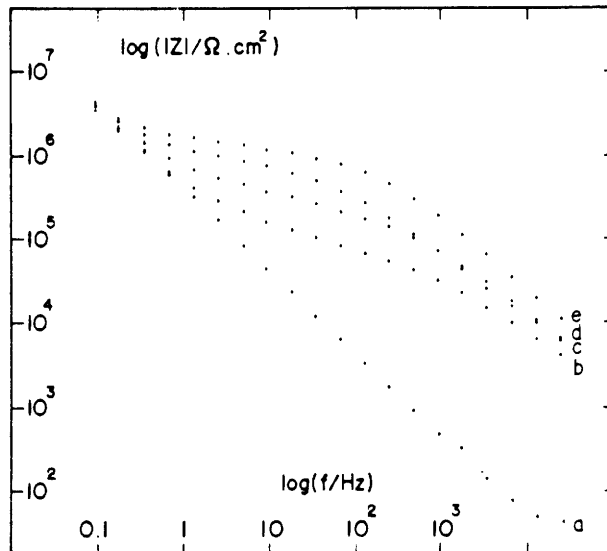
Typical Bode plots of the 1050 Al-alloy showing the variation of the impedance modulus,  $|Z|$ , vs.  $\log f$ , for different sealing times per unit oxide layer thickness, in the  $0 \leq t_s/\text{min } \mu\text{m}^{-1} \leq 3$  range, after anodizing in solutions A and B are depicted in Figs. 1 and 2, respectively.

The impedance spectrum for non-sealed porous oxide layers reveals a single capacitive contribution, as it can be seen in curves a in both Figs. 1 and 2. As it is well known, the effect of sealing in hot water involves the hydration of the outer porous oxide layer. Consequently, the hydrated alumina should occupy a greater volume fraction, blocking the pores and, thus, increasing the protective action of the coating. Figs. 1 and 2 show clearly that for increasing sealing time per unit oxide layer thickness the impedance spectra progressively exhibit a new capacitive contribution. This capacitive behaviour which occurs at high frequencies can be associated with hydration processes taking place at the outer portion of the porous layer structure. At the intermediate frequency region,  $|Z|$  exhibits a plateau separating the previously referred capacitive contribution from the dynamic response of the thinner underlying barrier layer, whose physicochemical properties remain practically unaltered after the sealing procedure, even for large,  $t_s$  values.

The whole set of experimental data for sealed porous



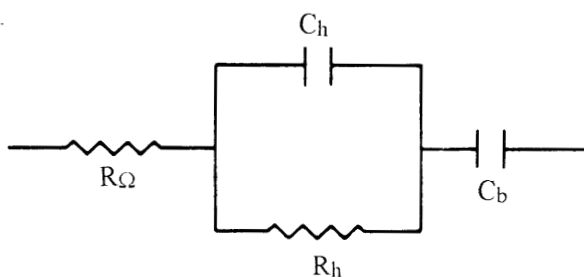
**Figure 1.** Influence of sealing time per unit thickness ( $t_s$ ) on the Bode plots corresponding to the Al alloy 1050 anodized in solution A.  $t_s/\text{Min } \mu\text{m}^{-1} = 0$  (a); 0.5 (b); 1.0 (c); 2.0 (d); and, 3.0 (e).



**Figure 2.** Influence of sealing time per unit thickness ( $t_s$ ) on the Bode plots corresponding to the Al alloy 1050 anodized in solution B.  $t_s/\text{min } \mu\text{m}^{-1} = 0$  (a); 0.5 (b); 1.0 (c); 2.0 (d); and, 3.0 (e).

oxide layers can be successfully interpreted by the transfer function corresponding to the electric circuit of Fig.3, which includes the series combination of  $R_\Omega$ , the ohmic resistance,  $C_b$  the barrier layer capacitance, and the  $C_h$ - $R_h$  parallel combination related to the hydrated porous layer. The  $R_h$  values were found to be about  $10^6 \Omega \text{ cm}^2$ , whereas those of  $C_h$  diminished, as it could be expected, as hydration proceeded, from ca. 2 nF cm<sup>2</sup> to 0.6 nF cm<sup>2</sup> for  $t_s$  values of 0.5 min  $\mu\text{m}^{-1}$  and 3 min  $\mu\text{m}^{-1}$ , respectively. It is worth noting that all  $C_b$  values were close to 0.4  $\mu\text{F cm}^{-2}$ .

Likewise, no influence of boric acid (usually employed as thermoinhibitor agent) was found, since the impedance spectrum profiles were insensitive to its addition to the sulphuric acid anodizing solution.



**Figure 3.** Equivalent circuit corresponding to the transfer function used to fit the experimental data presented in Figs. 1 and 2.

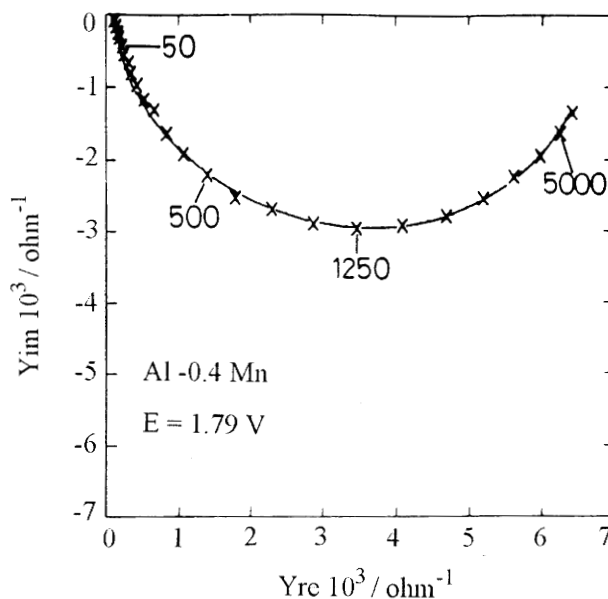
2. *Barrier oxide layers:* anodic films whose thicknesses increase linearly with applied potential are denoted as barrier layers. Their dielectric constant is about 8-9. The formation of barrier-type oxide layers takes place preferentially in electrolytes such as boric acid, ammonium borate, tartrate and citrate, and very diluted sulphuric acid, where, the dissolution rate of the oxide is rather low.

The admittance diagram of the binary alloy Al-0.4% Mn anodized in solution C at the oxide formation potential  $E_f = 1.79$  V is presented in Fig. 4. The corresponding transfer function used the non-linear least square fitting shown in this figure is:

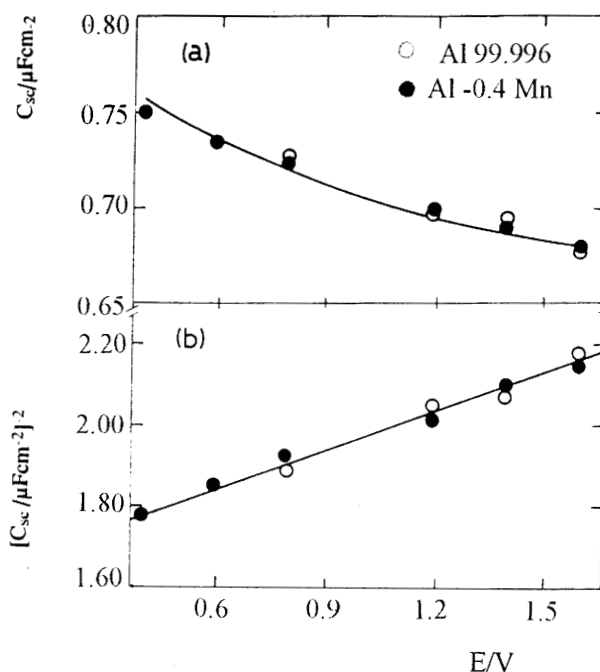
$$Z = R_h + [R_p^{-1} + j\omega C_{ss}(1 + j\omega P_{ss}C_{ss})^{-1} + j\omega C_{sc}]^{-1}$$

where  $R_p$  denotes the high resistance required to model the dark faradaic current,  $C_{sc}$  the capacitance of the space charge in the oxide layer which predominates at short relaxation times, and  $P_{ss}C_{ss}$  can be related to the time constant of the charge accumulation modes due to surface states. Obviously, the contribution of the capacitance of the Helmholtz layer,  $C_{DL}$ , was neglected in comparison to above mentioned capacitances. This assumption was justified taking into account the  $C_{sc}$  and  $C_{ss}$  values resulting from the fitting which were lower than the conventional value attributed to  $C_{DL}$ , as well as the good agreement between experimental and fitting data (see Fig. 4)

The dependences of  $C_{sc}$  on potential and the corresponding  $C_{sc}^2$  vs.  $E$  Mott Schottky plots, obtained for both high purity Al and the binary alloy Al 0.4% Mn previously anodized at  $E_f = 1.79$  V to attain a constant oxide thickness, are shown in Fig. 5. From these results, which clearly characterize a n-type semiconductor behaviour of the barrier oxide layer, it is possible to determine the donor concentration in the space charge,  $N_D \approx 10^{19}$  cm<sup>-3</sup>, and the flat band potential,  $E_{FB} \approx -3.9$  V, for the barrier oxide layers generated on both working electrodes. The value of  $E_{FB}$  agrees with the one obtained from photoelectrochemical measurements for these systems<sup>9</sup>. The present results sug-



**Figure 4.** Admittance diagram of the binary alloy Al-0.4% Mn anodized in solution C. Experimental (x symbols), and simulated (full line) data.

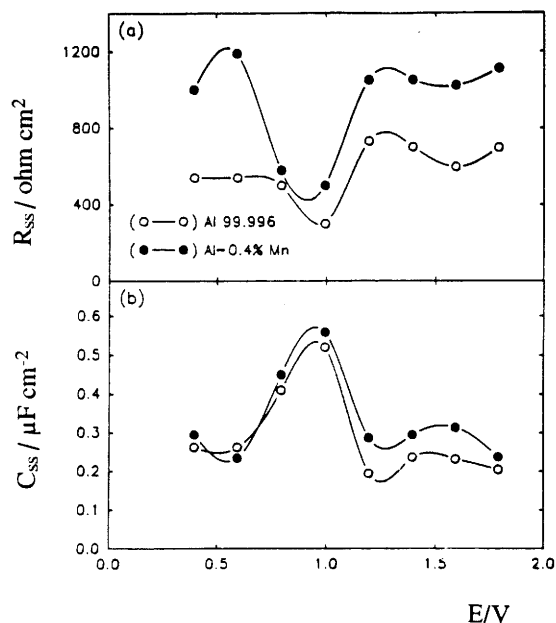


**Figure 5.** Dependences of  $C_{sc}$  (a) and  $C_{sc}^2$  (b) on potential for Al 99.996% (● symbols and binary alloy Al-0.4% Mn (○ symbols) anodized in solution C.

gest no participation of deep donor levels in equilibrium within the analyzed potential range. Thus, the charge distribution in the depletion layer can be associated only with shallow donor levels.

The strong dependences of the values of  $P_{ss}$  and  $C_{ss}$  on potential can be clearly seen in Fig. 6. The maximum in the  $C_{ss}$  vs.  $E$  plots confirms the existence of surface states in the oxide, whose energy level with respect to the conduction band limit is well defined by the value of the potential

corresponding to this maximum. These surface states can be probably associated with the electrode surface treatment carried out previous to the anodization, which for the present study consisted of mechanical polishing using 600 grade emery paper and 1.0, 0.3, and 0.1  $\mu\text{m}$  alumina acetone suspensions, followed by thorough rinsing with triply distilled water.



**Figure 6.** Dependences of  $R_{ss}$  (a) and  $C_{ss}$  (b) on potential for the systems described in Fig. 5.

## Conclusions

Dynamic system analysis using electrochemical impedance spectroscopy to study both anodically formed porous and barrier oxide layers on various aluminium substrates allowed to characterize the surface as well as the bulk properties of these layers produced in different aqueous electrolyte solutions. Particularly, the obtained results provide valuable information on the gradual hydration of the porous oxide layers due to different sealing times per unit thickness of the oxide. Furthermore, the electronic properties of the n-type semiconducting thin barrier layer could be also derived from the impedance spectra.

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