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Adsorption of organic compounds at the aluminium oxide/aqueous solution interface during the aluminium anodizing process

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ABSTRACT

The paper reports a systematic study concerning the role played by different organic compounds (glycolic acid, oxalic acid, glycerol) on the electrochemical oxidation process of aluminium in sulphuric acid solution. The result of the experiment as a whole provides a clear indication of the deep influence exerted by the three selected organic compounds on the aluminium oxide structure, leading to the formation of a more compact oxide layer. Electrochemical impedance spectroscopy results appear of particular interest; they are discussed in the light of a model proposed by Bojinov. The relevant parameters, half-jump distance *a* and cross-capture section *S*, are found consistently related to variations in the oxide structure (porosity). This gives a sounder basis to the physically correct nature of the assumptions underlying the Bojinov model, also suggesting that organic compounds are adsorbed at the aluminium oxide/aqueous solution interface.

1. Introduction

Study of the physico-chemical properties of aluminium oxide should be framed within a more general endeavour by scientists aiming to develop a model able to rationalize the formation of oxide films on the so-called 'valve' metals: Ti, Zr, Bi, Ta, Nb, etc. [1]. Recent theoretical proposals presented in literature appear quite promising for the study of this topic; they are based on the identification of three spatial regions between the metal and the solution: the metal film interface, the film itself, and the film's electrolyte interface. Therefore, the total potential difference is assumed to be distributed on these three interfaces [2–9].

The high field model (HFM), as proposed by Verwey, Cabrera and Mott (see Ref. [2] and references therein), accounts for the growth of oxide films on typical valve metals [10,11] as well as non-typical valve metals such as Sn [12] and In [13] under galvanostatic control. The HFM model assumes that the anodic oxide film grows following the outward movement of interstitial cations under the influence of the applied electric field; this "driving force" decreases as the film grows thicker. Moreover, in the HFM approach it is hypothesized that the film does not dissolve and that film growth occurs only at the film/solution interface [10,13].

Macdonald proposes a model accounting for the diffusivity of anionic vacancies within the growing oxide layer, which is based on the point defect model (PDM) in conjunction with a Mott–Schottky analysis [8,9].

In the case of aluminium, a model describing the growth of the oxide film should feature reactive processes occurring both in the passive oxide film and at the various interfaces. In fact, Al oxidized at the metal-oxide (M/O) interface (as for the Al dissolution in water) yielding $A1^{3+}$ ions; so a double layer is localized at the (M/O) interface, where the aluminium oxide acts as a solid electrolyte. The relevant diffuse double layer thickness is assumed to be small, being mainly determined by the Helmholtz layer [14]. While at the oxide-solution (O/S) interface, oxygen ions enter the oxide layer framework [15]. Following Valand and Heusler, oxygen ions can be formed on the basis of reactions (Rl)–(R3) [16]:

$$H_2O = OH^-_{(ad)} + H^+ \quad (R1)$$

$$OH^-_{(ad)} = O^{2-}_{(ad)} + H^+ \quad (R2)$$

$$O^{2-}_{(ad)} \rightarrow O^{2-}_{(ox)} \quad (R3)$$

Reaction (R3) is assumed to be the rate-determining step: adsorbed oxygen ion crosses the O/S interface before incorporation in the oxide matrix. Thus, aluminium and oxygen ions diffuse through the oxide layer, then aluminium ions will reach and dissolve in solution at the O/S interface, while the oxygen ions diffuse from the O/S to the M/O interface. The thick aluminium oxide

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layer behaves as an insulator with a dielectric constant varying between 7.5 and 12 [17]. In the case of an anodic polarization of 1 V, the electric field strength present in an oxide layer 10 nm thick is about 1 mV cm^{-1}. Thus, migration is the driving force for ionic transport through the oxide. This picture, drawn on the basis of simple electrostatic considerations, is supported by experimental evidence, where field strengths are found ranging between 10^6 and 10^7 V cm^{-1} [14,17]. In particular, in the case of aluminium anodizing, the ionic transport number of aluminium ions is about 0.4 and that of oxygen ions about 0.6, and both cations and anions are expected to contribute to the film growth [18].

Recently, the aluminium electro-oxidation process appears as a further challenging subject, with several interesting topics still open to discussion, relating to the properties of aluminium oxide and its protective quality as a function of different anodizing process conditions [14,19–23]. Al_2O_3-coating on layered $LiCoO_2$ is a promising material to improve the performance of cathodes in rechargeable lithium batteries [24]. Sulphate anion incorporation in porous anodic alumina and their dependence on the thermodynamic and transport properties of cations has been discussed in relation to the structure of the porous oxide [25], due to its interest also as a material structured on a nanometric scale. The mass-fractal-like microstructure and proton disorder in nanostructured pseudobohemite has been studied by using neutron-scattering [26].

In this perspective, the aim of the present paper is to investigate the influence of organic compounds on the overall electrochemical oxidation process of aluminium.

To this end, we studied the influence of glycerol, glycolic acid and oxalic acid; they were selected because of their structural characteristics and possible use in industry, in an attempt to improve the compromise between oxide quality and process efficiency. Potentiodynamic and chronoamperometric curves and impedance spectra, collected in a fairly wide range of potential (0–5 V *vs.* SCE) are presented and discussed, allowing the influence of adsorption of organic compounds at the O/S interface to be assessed. For the sake of comparison, information on the pore size is also obtained by UV/vis reflectance spectroscopy and transmission electron microscopy (TEM) micrographs.

2. Experimental

Aqueous solutions of H_2SO_4 2.0 M (Aldrich Chem. Co.) featuring different organic compounds (oxalic acid, Carlo Erba R.P.E., glycolic acid, Fluka Chemika and glycerol, Carlo Erba R.P.E.) at various concentrations, were prepared by using Millipore MilliQ reagent grade water.

Potentiodynamic (j *vs.* E) and chronoamperometric (j *vs.* t) curves were recorded by using an Ecochemie PGSTAT 20 connected to a conventional three-electrode cell system. The working electrode was prepared by cutting Sigma–Aldrich 99.999% aluminium rods of 6.35 mm radius. Aluminium surfaces were mechanically polished by using a Buehler Minimet 1000, equipped with Buehler emery paper and alumina (0.05 μm). If necessary, prior to every electrochemical measurement, an electropolishing procedure was applied (anodic polarization 4.0 V *vs.* SCE for 30 s in HNO_3 10 mol dm^{-3} solution, RDE 500 rpm [27]). A platinum sheet and a saturated calomel electrode (SCE) were used as counter and reference electrode respectively.

Impedance spectra were collected in the 65 kHz to 25 mHz frequency range, the peak-to-peak amplitude of the sinusoidal signal was 5 mV. The measurements were made by using a Solartron 1286 Electrochemical Interface and 1250 Frequency Response Analyzer. Fitting of EIS spectra was performed by using the LEVM (version 8.05) Complex Nonlinear Least Squares Fitting Program.

A Metrohm 628 RDE (rotating disk electrode) allowed potentiodynamic curves to be recorded as a function of the working electrode angular rotation rate.

All the potential values reported in this paper refer to the SCE. The temperature was maintained constant, by using a Haake thermostat, at 298 ± 0.1 K.

Tribological tests were carried out by using aluminium surfaces, 0.015 m^2, which had been oxidized under galvanostatic control (1.5 A dm^2) at 293 K for 50 min, in H_2SO_4 2.0 mol dm^{-3}, oxalic acid 0.65 mol dm^{-3}, glycolic acid 0.65 mol dm^{-3} and glycerol 2.0 mol dm^{-3} aqueous solution. In some cases samples were sealed in a boiling water bath: at 370 ± 3 K for 60 min. The hardness was measured by using a REMET HX-1000 apparatus with a 0.098 N load and 10 s indentation time. The indentation was performed on a section of the oxide surface, which was previously obtained by a sample embedded in epoxidic resin, cut and polished by using a REMET Micromet and mechanically polished by using a Buehler Minimet 1000, with Buehler emery paper and alumina 0.05 μm. Oxide thickness was measured by using a SONATEST instrument. The apparent density was determined from the W/AT ratio: A sample area, T and W are the thickness and weight of the oxide layer, respectively. W values were obtained by weighing the sample before and after the oxide dissolution in a CrO_3 (Aldrich Chem. Co.) 0.2 mol dm^{-3}/H_3PO_4 (Carlo Erba R.P.E.) 0.5 mol dm^{-3} aqueous solution at 333 K. Weight loss measurements were performed following the ISO 3210 standard procedure, values are reported as a weight loss per surface unit (mg cm^{-2}).

A quantitative estimation of the porosity of the film was carried out by recording UV–vis spectra under reflection conditions. The method relies on the determination of a UV–vis spectrum of the sample before and after an immersion of 48 h in a 10% methylene blue aqueous solution [28]. To this end, a Perkin-Elmer (Lambda 19, Illuminant D65, Observer: 10°) UV–vis spectrophotometer with analytical software for colour measurements was used. L^*, a^*, b^* colour parameters were determined following the CIE (Commission International de l'Eclairage) colorimetric method. In this method, L^* is the lightness axis (black 0, white 100), a^* is the green ($-a^*$) to red ($+a^*$) axis, and b^* is the blue ($-b^*$) to yellow ($+b^*$) axis.

A JEOL 2010 (200 kV) transmission microscope was used for microstructure observations, the images were obtained using a Slow Scan Camera GATAN, the oxide film thickness was reduced in a DuoMill GATAN ion-beam.

3. Results and discussion

3.1. Potentiodynamic results

Fig. 1 (solid line) shows a potentiodynamic curve of an aluminium electrode in H_2SO_4 2.0 mol dm^{-3} aqueous solution: a first broad oxidation peak is centered at about 0.5 V (*region* 1), which is followed by an almost constant current 'plateau', in the 1–2 V potential range (*region* 2), then the current density increases almost linearly while scanning the more anodic potentials up to 4 V (*region* 3). The backward scan is characterized by a constant and very low value of current, indicating that the electrochemical processes active between −0.5 and 4 V are of irreversible nature.

On the basis of models present in the literature the following processes can be tentatively assigned as relevant to the three different regions found in the potentiodynamic curves [1]. *Region* 1: Al oxidation reaction: $2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$. *Region* 2: passive film growth, with an increase in the film (barrier layer) thickness. *Region* 3: simultaneous formation and dissolution of the porous oxide layer (the increase in the current density is due to an increase in the active electrode surface).