

Impedance spectroscopy study of anodic growth of zirconium oxide film in NaOH medium

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The growth of anodic oxide films on zirconium metal has been followed up to 300 V by electrochemical impedance spectroscopy and scanning electron microscopy. The maximum layer thickness is 720 nm, the dielectric constant of the film is measured at 19.5 and the growth constant is 2.4 nm V⁻¹. Above 50 V, the presence of two impedance relaxations between 1 Hz and 200 kHz reveals a bilayered structure. This may be a consequence of a lower resistivity of the outer layer induced by some electrolytic solution infiltration into film defects.

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1 Introduction

 ZrO_2 is an insulator compound with a large bandgap at 5 eV [1]. This oxide present potential applications in various fields such as a protective coating [2], dielectric compound in MOS devices or as high temperature O^{2-} conducting electrolyte, important in sensors and fuel cell applications [3]. The growth of thick oxide films can be obtained by sputtering, pulsed laser deposition, chemical vapor deposition, atomic layer epitaxy [3] and also by wet methods such as anodization in which the metal, used as an anode, is oxidized electrochemically in an electrolytic solution [4, 5]. In the case of dielectric oxide films, a high electric field must be maintained in the layer in order to control the kinetic of the growth by anodization. It is well-documented that in the case of zirconia the growth rate is almost exclusively limited by O^{2-} migration from the film/electrolyte interface towards the metal/oxide interface where O^{2-} reacts with the oxidized zirconium, Zr^{4+} . The transport number of Zr^{4+} is almost null [4, 5].

$$Zr \Rightarrow Zr^{4+} + 4e^{-}, \tag{1a}$$

 $Zr^{44} + 2O^{2-} \Rightarrow ZrO_2.$ (1b)

In the present paper we take the case of the anodic growth of zirconia in NaOH since this medium is known to give rise to non-contaminated oxide films [6]. We describe a non-destructive procedure, based on electrochemical impedance spectroscopy (EIS) measurements, to follow the variation of layer thickness and microstructure with the applied potential.

2 Experimental

The electrodes were zirconium rods of purity 99.8% (Goodfellow), 1.5 mm in diameter and 5 to 10 mm in length (the electrode surface areas exposed to the electrolyte were ranging between 0.25 and 0.5 cm²).

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They were sealed in a glass tube with an epoxy resin. Several sealing modes were tested but this configuration gave the best results in terms of highest voltage attained. After a first mechanical polishing with P400 and P1200 abrasive paper they were finally polished with a 3 µm diamond powder on a metallurgical cloth. Then the electrodes were degreased in acetone and ethanol 5 minutes each in an ultrasonic bath before to be chemically etched 2 minutes in a solution of (1:15:34) volume mixture of reagent grade 48% HF:68% HNO, : Millipore quality water. After the etching, an impedance spectrum was recorded at a potential close to the rest potential, that is -1 V vs. MSE (for mercurous sulfate electrode, with a potential of +0.65 V vs NHE) in the anodization medium in order to control the initial electrode surface state. The surface capacitance of the etched electrode was determined from this spectrum. An etched electrode was used only once and each new experiment was performed with a new rod. The aqueous electrolytic solution was 0.1 M NaOH (reagent grade, Prolabo) (pH 13). The anodization was performed in a two electrodes configuration, the counter electrode being a cylindrical titanium grid covered by an IrO, coating. The Zr rod was placed in the center of the cylinder. The applied potential during anodization, noted E, will be referred to the IrO₂ electrode. The solution was stirred with a magnetic barrel. The potential sweep was started at 0 V vs. IrO, and performed at a constant sweep rate, noted $v_{\rm o}$, classically 100 mV s⁻¹ or 25 mV s⁻¹ with a Keitley 2410 sourcemeter. The voltage sweep was stopped at different potentials and an impedance spectrum was recorded at 0 V vs. MSE. The voltage sweep was then continued and so on. The AC measurements were done with an EG & G PAR 283 potentiostat combined with a Solartron 1255 model frequency response analyser both monitored by the Zplot-2 software from Scribner Associate. The frequency range was 1 or 10 Hz to 200 kHz with 10 points per decade. The AC amplitude was 30 mV. The spectra were fitted and analysed with help of the Zview-2 software package. The layer cross sections were observed with a scanning electron microscope (SEM) (Stereoscan 440 from Leica).

3 Results and discussion

In Fig. 1 is presented the variation of the current density with the potential for two different scan rates, 25 mV s^{-1} and 100 mV s^{-1} . The breakdown occurs at 300 V where a dramatic increase of the current density is observed and the anodisation can not be continued. The breakdown is not due to film homogeneous failure but to an intense corrosion localized near the seal (seal failure). The electrolytic solution is brought in contact with the bare metal and a violent current leakage is produced. During this process a flame is observed, located in the vicinity of the epoxy seal.

A large current peak (noted A) is observed at low voltage which can be ascribed to the oxygen evolution reaction occurring before the passivation of the surface. Afterwards, the current density is not constant but slowly increases with applied voltage. The maximum current density, *j*, at 100 mV s⁻¹ before the



Fig. 1 Variation of the current density during a potential scan at 100 mV s⁻¹ (+) and 25 mV s⁻¹ (×).

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Fig. 2 (a) Bode representation of the effect of the increasing applied voltage (etched, 50 V, 100 V, 200 V and 295 V) on the impedance; (b) equivalent circuit used for the analysis of the EIS response of the two layered film; (c) high frequency approximation.

breakdown is 2.5 mA cm⁻². Figure 1 also reveals that *j* is not proportional to the scan rate as expected in the case of a high field [7] or point defect [8] processes, but only decreases slightly at the lower sweep rate (25 mV s⁻¹). This assumes the involvement of side reactions and low faradaic efficiency of the process.

The variation of the electrical ac-response of the electrode has been followed with increasing the applied voltage applied (Fig. 2a). At 50 V two relaxations appear which become better-defined at higher voltage. We can notice that at frequencies above 100 Hz the impedance increases with E. This suggests that the growing anodic oxide layer is observed in this frequency range. Whereas below 100 Hz, the impedance modulus poorly changes with the voltage up to 295 V. This behaviour can be explained by a bi-layer model with dense inner layer and porous outer layer of lower resistivity. This may be due to infiltration of the electrolytic solution at the grain boundaries. R_2 is the resistance of the outer layer, and R_1 is a series resistance that contains the metal contribution, electrical contacts and electrolytic solution resistances.

At frequencies above 5 kHz R_2 contribution becomes negligible. If we assume that the dielectric behaviour of outer layer is the same as that of the inner one (they are made of the same material, zirconia), we can simplify the equivalent circuit into that presented in Fig. 2c. The problem here is to extract the film capacitance, C_f and to get rid of the dispersion phenomena. It is important to note that the approach used in a previous paper to analyse layers obtained at high temperature and high pressure and demonstrating a variation of ε with the frequency, failed to describe the present EIS data [2]. This is shown in Fig. 2a where the slope of the high frequency part of the impedance modulus does not vary with the frequency.

Therefore we have used an approach first proposed by Brug et al. [8] in the case of a capacitance affected by a.c. frequency. In the present case, we have supposed that the dielectric layer is not the double layer as in Ref. [8] but the oxide film. The impedance of CPE₃ is written $Z = [A_3(j\omega)^n]^{-1}$, with 0.5 < n < 1. A_3 is a constant and the CPE acts like a capacitor when n is equal to 1. Value of n varies slightly with *E*, ranging between 0.94 and 0.98. The total film capacitance is obtained by:

$$C_f = [A_3(R_1)^{1-n}]^{1/n} . (2)$$

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Fig. 3 Cross-sectional SEM view of a 500 nm thick

film grown at 225 V (sweep rate 100 mV s⁻¹)



The film thickness is given by:

$$d = \frac{\varepsilon \varepsilon_0 S}{C_f} \; .$$

(3)

Where ε_0 is the permittivity of vacuum (8.85 × 10⁻¹⁴ F cm⁻¹), ε the dielectric constant of the oxide and *S* the real surface area which includes the roughness factor. SEM views of the electrode surface show that the surface roughness of the samples was low and we retain a value of 1 in the following.

However, in Eq. (3) ε is an unknown parameter. The values reported in the literature vary in a very large range domain, from 21 [4, 10] to 38.3 [11] and are described to depend upon the growing electrolyte used since some anions can be inserted in thick zirconium oxide layers [3, 12, 13]. Anodization in NaOH produces a non contaminated zirconium oxide film [13]. ε has been determined from the film thickness determined by direct SEM observation of anodised rod cross-sections (Fig. 3). The samples have been observed in the backscattering mode and the superficial oxide layer appears darker if compared to the metal (Fig. 3). As shown in Fig. 4, the best fit between EIS and SEM data has been obtained for $\varepsilon = 19.5$. We can note that high calculated dielectric constant seems sometime due to an overestimation of the film thickness measured from the charge exchanged (e.g. [7]) whereas side reactions can occur and the faradaic efficiency of oxide film growth is generally lower than 1 as shown below. Figure 4 shows that there is no influence of v_b on both ε and the growth rate. The film thickness varies linearly with the applied voltage and the growth constant is 2.4 nm V^{-1} . The thickness of the dense layer measured at 50 V is thus equal to 110 nm (Fig. 4) and increases slightly at higher voltage when the porous layer is present. Since the breakdown occurs at 300 V, the maximum total film thickness in NaOH is about 720 nm. The electric field in the film during the growth is very high and constant, measured at 4.2×10^6 V cm⁻¹ if we neglect the potential drops at the interfaces. The Faradaic efficiency of the growth measured at 290 V and 100 mV s⁻¹ is 23% with a theoretical thickness at 3.1 μ m and an experimental one at 0.72 μ m.



Fig. 4 Variation of film thickness with applied voltage, as deduced from EIS measurements: (+) $v_b = 25 \text{ mV s}^{-1}$; (×) $v_b = 100 \text{ mV s}^{-1}$ and SEM observation: (•) $v_b = 100 \text{ mV s}^{-1}$; (**m**) $v_b = 25 \text{ mV s}^{-1}$.

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Fig. 5 Schematic view of the microporous layer (arbitrarily scale).

By further analyzing the EIS spectra, we can get information on the porous layer characteristics. Figure 5 shows a schematic cross-sectional view of the porous layer. The porosity will be estimated considering that the film contains pores which are oriented perpendicular to the electrode surface and filled with the electrolytic solution. The mean pore section area is *s* and the number of pores per square centimeter is *n*. d_m is the thickness of the microporous layer. The volume of pore per square centimeter is *ns* d_m and the electrical resistance of the pores is given by: $R_2 = d_m/\sigma ns$, with σ the conductivity of the electrolytic solution which fills the pores. The fraction of surface and volume occupy by the pores, η , is given by:

$$\eta = ns = \frac{d_m}{\sigma R_2} \ . \tag{4}$$

In the case of a film grown in 0.1 M NaOH at 250 V, we have $R_2 = 23 \text{ k}\Omega \text{ cm}^{-2}$ (the plateau observed on the modulus curve in Fig. 2a around 100 Hz corresponds to $R_2 + R_1$), $\sigma = 0.02 \text{ S cm}^{-1}$ and $d_m = 580 - 110 = 470 \text{ nm}$. We obtain a very low value, $\eta \approx 10^{-7}$, in agreement with the fact that the bilayered structure is not observed on SEM views. Accordingly, the pores may be very thin and their density very low. Further study of the film structure, by transmission electron microscopy for instance, would be necessary to validate the present model.

In summary, we have studied by impedance spectroscopy and SEM the growth of anodic films of zirconia in 0.1 M NaOH. In spite of several attempts to improve the sealing by testing some other sealing modes, we have not been able to go beyond 300 V. By taking 19.5 for the dielectric constant of ZrO_2 we have found a very good correlation between the EIS thickness measurements (using the method described by Brugg et al. to determine the film capacitance) and direct observation of film cross-section. EIS also shows that the film is composed of two layers with different electric behaviour. These results suggest that some very fine porosity is present in the outer layer and that the electrolytic solution could be infiltrated into defects present in the film such as micropores. However, this hypothesis remains to be validated by the direct film observation.

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