Synthesis of nanostructured zirconia by anodization at low potentials

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This work reports the synthesis of nanostructured ZrO_2 by anodization of zirconium electrodes at potentials well below the range of 10–50 V used as a standard procedure. Zirconium was first anodized in a 1M $(NH_4)_2SO_4$ electrolyte and then further anodized in the presence of fluoride ions added to the electrolyte as NH_4F. The maximum potential applied to zirconium during the whole process was 1 V with respect to an Ag/AgCl (sat.) reference electrode. Amorphous films of ZrO_2 consisting of nanopores and nanowire-like structures were produced with this low-potential methodology.

1 Introduction

Self-ordered arrays of ZrO_2 nanotubes present a high surface-volume ratio and their fabrication attracts a considerable scientific interest due to their wide range of potential applications as catalyst support structures [1, 2], sensors [3] or as solid-state electrolytes [4–6]. Electrochemical anodization of zirconium in aqueous electrolytes containing fluoride ions has proved to be an effective method for the synthesis of ZrO_2 nanotube arrays [7–18]. Electrolytes used include H_2SO_4, $(NH_4)_2SO_4$ and Na_2SO_4, while fluoride ions are introduced as NH_4F or NaF. The most common procedure involves the initial application of a potential sweep from the open circuit potential (OCP) until reaching a desired potential value in the range 10–50 V, which is then maintained constant for several hours [16]. In some cases, however, zirconia is directly anodized to a high potential value [8, 15]. Highly ordered ZrO_2 nanotube arrays have been already grown with these electrochemical methodologies [11, 17, 18].

The shape, size and crystallinity of the formed ZrO_2 nanotubes is strongly dependent on the value of the final potential applied [9, 15]. However, its influence has been only studied at potentials over 10 V. In addition, it

has been observed that the morphology of the obtained nanotubes is also influenced by the sweep rate at which the potential is increased from the OCP to the final anodic potential [14]. This indicates that the initial stage in which zirconium is exposed to low anodic potentials plays a relevant role in the formation of the nanotubes. Nevertheless, there are no reports in which the initial stages of formation of zirconia nanotubes at low potentials are investigated in detail.

The present work reports a first study on the synthesis of nanostructured ZrO_2 films in the aqueous system $(NH_4)_2SO_4 - NH_4F$ by the anodization of zirconium electrodes at low potentials, only up to 1 V vs Ag/AgCl(sat).

2 Experimental

Experiments were conducted in a thermostatized three-electrode electrochemical cell using a 1 mm thickness zirconium plate as working electrode (99.8 %, Johnson Mathey), a platinum flag made of platinum foil as the counterelectrode, and an Ag/AgCl(sat.) reference electrode inserted in a Luggin capillary. Unless otherwise stated, all potentials reported in this work are given with respect to this reference electrode (standard potential +0.2 V vs. NHE).

The working electrode was made of a zirconium plate embedded in epoxy resin, leaving an uncovered

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surface of well defined area exposed to the electrolyte. This surface was successively polished with sandpaper grade 2500, then with diamond paste of 9 and 3 μm, and finally washed with ethanol and dried under nitrogen. The electrolyte was 1 M $(NH_4)_2SO_4$ prepared dissolving $(NH_4)_2SO_4$ (99.5%, Merck) in deionized water. In experiments including fluoride ions, this ion was added to the 1M $(NH_4)_2SO_4$ electrolyte as NH_4F (40 p/p, Nitine Inc.). The pH in the electrolyte was 6.2.

At the start of each experiment the electrolyte was initially de-oxygenated by bubbling high purity nitrogen. During the electrochemical measurements the cell was operated under thermostatic conditions at 30°C, keeping a flow of nitrogen over the electrolyte.

Zirconium electrodes were initially anodized at +0.8 V in the fluoride-free electrolyte during 1 hour. Afterwards, ammonium fluoride was directly added to the electrolyte in order to reach a concentration of 0.064 wt.% NH_4F. Then, after 1 minute of resting time in this electrolyte, the zirconium electrode was again anodized during a period of 30 minutes. The potentials applied during this second stage were +0.8, +0.9 and +1.0 V. In this two-steps method, the initial anodization step in the fluoride-free electrolyte helped to improve the homogeneity of the initial oxide layer on which the nanostructuration process would occur.

Samples of the zirconia films formed both after the initial anodic pulse in the fluoride-free electrolyte and after the second anodic pulse in the fluoride-containing electrolyte were washed in distilled water, dried and kept in nitrogen for SEM, XDR and TEM analysis. Electrochemical experiments were conducted using a BAS 100 electrochemical interface operated with a personal computer. The structure and morphology of produced zirconia films were characterized using a FEI SEM Inspect F-50 model Field emission gun scanning electron microscope (FE-SEM) and a FE-SEM Magellan 400. The crystallinity was characterized with XRD using a Brucker D8 diffractometer with CuKα1,2 radiation in both the conventional θ-2θ and grazing angle configurations. The samples were also analyzed in HRTEM and HAADF STEM modes using a FEI Titan 80–300 electron microscope. The microscope was operated at 300 keV and equipped with an Oxford Inca EDX detector. A TEM cross-sectional sample that included the Zr-ZrO_2 interface was prepared from the top surface by Focus Ion Beam (FIB) using FEI Helios SEM/FIB dual beam equipment.
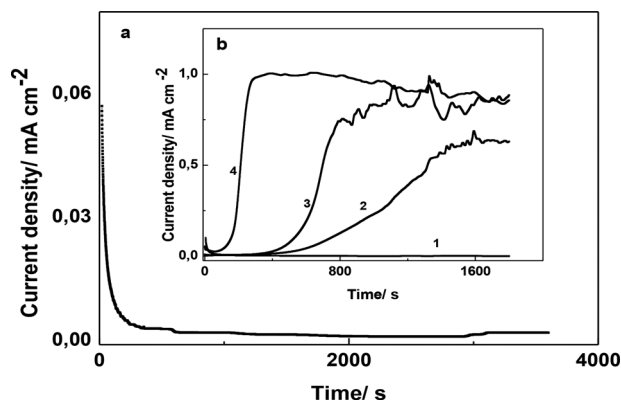

Fig. 1 Current density transients obtained during the anodization of zirconium. (a) in fluoride-free electrolyte (+ 0.8 V); (b) in electrolyte with fluoride ions at +0.8 V (curve 2), +0.9 V (curve 3) and +1.0 V (curve 4). Curve 1 in this figure corresponds to the same current density transient presented in figure 1(a).
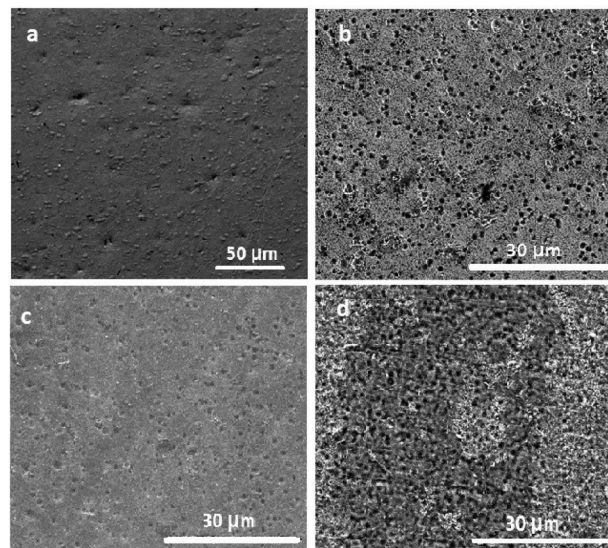

Fig. 2 SEM top views of the oxidized layers formed on zirconium. (a) +0.8 V in fluoride-free electrolyte; (b) +0.8 V with fluoride ions; (c) +0.9 V with fluoride ions; (d) +1.0 V with fluoride ions.

3 Results and discussion

Figure 1(a) shows the potentiostatic current density transient obtained during the anodization of zirconium during 1 hour at +0.8 V in the fluoride-free electrolyte. The continuous decay of current in time can be associated to the formation of a continuous ZrO_2 layer which offers a resistance to the transport of ions that increases with time as the film increases its thickness. SEM micrograph in figure 2(a) shows a top view of the produced ZrO_2 film.

The formation of this film would occur according to the following anodic reaction [9]:

$$Zr + 2H_2O \rightarrow ZrO_2 + 4H^+ + 4e^- \tag{1}$$
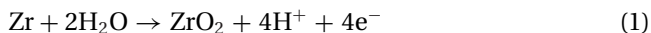
According to this reaction, calculating the total charge density from the current density transient in figure 1(a) and assuming a density of 5.68 g cm^{-3} for ZrO$_2$, the thickness of the formed film was estimated to be 0.26 μm.

Figure 1(b) shows the potentiostatic current density transients obtained when the ZrO$_2$ film initially formed in the fluoride–free electrolyte was subjected to further anodization at various potentials in the electrolyte containing 0.064 wt.% NH$_4$F. When comparing current density transients obtained in both electrolytes at +0.8 V (curves 1 and 2 in figure 1(b)), it can be seen that the presence of fluoride ions contributes to a notable increase of the anodic current density with respect to the one obtained in the fluoride-free electrolyte. The increase in current density starts earlier and becomes more pronounced when the potential applied to the working electrode in the fluoride containing electrolyte is successively increased to +0.9 and +1.0 V (curves 3 and 4 in figure 1(b), respectively).

The presence of fluoride ions in the electrolyte also had an important effect on the surface morphology of the ZrO$_2$ films obtained after being further anodized at +0.8, +0.9 and +1.0 V (see SEM micrographs in figures 2(b)–(d), respectively). This indicates that the rising section observed in the current density transients in figure 1(b) is to some degree related to the formation of pits triggered by the presence of dissolved fluoride ions in the electrolyte. The number of pits formed increases with the increase in the applied potential, which correlates well with the increase of current density observed in the respective current transients.

An additional effect of the presence of fluoride ions on the morphology of the ZrO$_2$ formed films can be observed in figure 3, which shows SEM observations of the same films in figures 2(b), 2(c) and 2(d), but at larger magnification. As it can be observed, all the ZrO$_2$ films anodized in the presence of fluoride ions present some degree of nanostructuration. At +0.8 V the nanostructuration is incipient and focalized in the base of pits which shows the growth of some wire-like structures (figure 3(a)). However, in this case there is still an important fraction of the initial ZrO$_2$ surface which is still not affected by pit formation. At +0.9 V there is a certain degree of nanostructuration which shows mainly in the form of nanopores on the surface and of nanowire-like structures inside the pits (figure 3(b)). At +1.0 V nanostructuration in the form of nanopores and nanowire-like
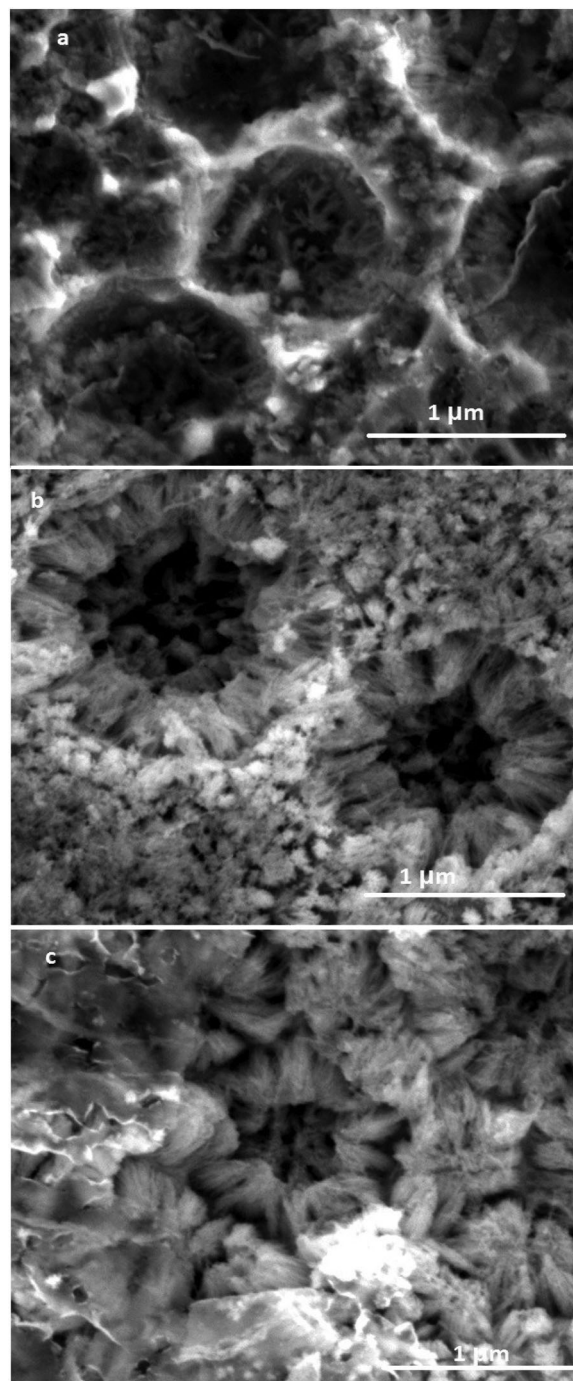

Fig. 3 SEM top views of the oxidized layers formed on zirconium in electrolyte with fluoride ions. (a) +0.8 V; (b) +0.9 V; (c) +1.0 V.

structures is widespread all over the film (figure 3(c)). In this last case, some small areas of the film can still be seen covered by a thin continuous film. This is presumably the remains of the oxide film initially formed at +0.8 V in the fluoride-free electrolyte.

ZrO_2 films formed at +1.0 V in the presence of fluoride ions, which presented the highest degree of nanostructuration, were further characterized to assess in more detail their structure, morphology and crystallinity. A high magnification FE-SEM micrograph of a pit zone is shown in figure 4(a). Bundles of nanowires, around 100 nm in diameter and aspect ratio 4–5, can be recognized. Figure 4(b) is a higher magnification image of one of the bundles in figure 4(a), which consists of many nanowires with length equal to the bundle length, around 400–500 nm, and thickness around 5 nm, so aspect ratio around 100. Formation of wirelike structures have been previously reported for the anodization of zirconium at 20 and 30 V in $(NH_4)_2SO_4 - NH_4F$ electrolytes [15].

A TEM image of a cross-section of this zirconia film is shown in figure 4(c). This image shows a film containing elongated vertical channels which are regularly distributed along its extension. Continuous parts of the film should correspond to zones formed by bundles of nanowire-like structures as those observed in figure 4(a) (FE-SEM image of the walls of a pit). Elongated vertical channels should correspond to nanopores such as those observed in the top-view SEM micrograph of this film (figure 3(c)).

Assessment of the crystallinity of this film was conducted by TEM. Selected Area Diffraction (SAD) image shown in insert of figure 4(c) indicates that the film is made of amorphous ZrO_2. This result was confirmed by grazing angle XRD analysis (not shown). The amorphous character of this film obtained at +1 V is consistent with the observed influence of potential on zirconia crystallinity. Previous studies reported that the crystallinity of zirconia films obtained in the $(NH_4)_2SO_4 - NH_4F$ electrolyte was drastically reduced when the anodization potential was decreased from 50 to 10 V [15]. The increase in current density obtained during the synthesis of zirconia nanotubes in the presence of fluoride ions has been attributed to the ability of fluoride ions to form water-soluble ZrF_6^{2-} complexes according to the following reaction [9]:

$$ZrO_2 + 6F^- + 4H^+ \rightarrow [ZrF_6]^{2-} + 2H_2O \qquad (2)$$
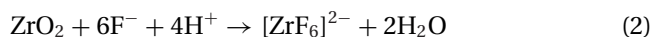
The rising part of the current density transients obtained in the presence of fluoride ions has been associated to the period of formation of an initial porous structure, the area of which increases with time. Similarly, the plateau of these current density transients has been associated to the formation and growth of nanotubes [9]. It has been observed that the addition of fluoride ions during anodization of zirconium at 20 V increases the
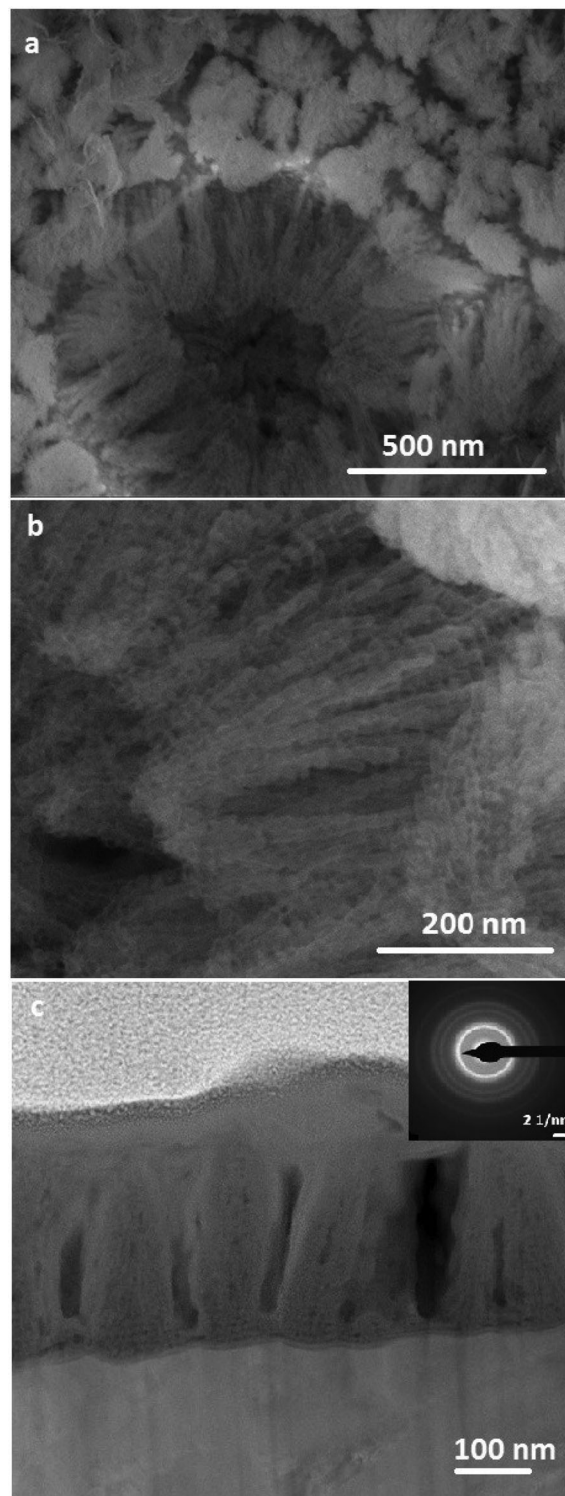

Fig. 4 (a) SEM top view of the oxide film formed on zirconium in electrolyte with fluoride ions at +1.0 V; (b) SEM view of one of the bundles of nanowire-like structures identified in a; (c) scanning TEM image showing cross section of the same film. The insert shows a Selected Area Diffraction (SAD) image. (See higher quality version of these images in Supplementary Material).

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current (ca.) five times with respect to the fluoride-free electrolyte [16]. In the present case, addition of fluoride to the electrolyte increased the plateau current density over 100 times with respect to the fluoride-free system. The effect of fluoride ions can be more clearly seen with the two-steps methodology, as in the second pulse fluoride ions start dissolving the initially formed zirconia layer.

The observed effect is remarkable considering that the fluoride concentration used in this work (0.064 wt.% NH_4F) is about ten times smaller than the one used in zirconia nanotubes synthesis at higher potentials (0.5 wt.% NH_4F). There are two main reasons which can explain the observed higher increase in the anodic current density: i) during anodization at low potentials the presence of fluoride ions contributes to a dramatic increase of the surface for ZrO_2 growth, which is reflected in the formation of a large number of pits and nanowire-like structures; ii) the ZrO_2 film initially formed at low potentials in the fluoride-free electrolyte is very compact, therefore the initial growth current on which the effect of fluoride ions is to be compared is relatively low (see curve 1 in figure 1(b)).

4 Conclusions

The results in this work prove that it is possible to synthesize nanostructured ZrO_2 films by anodization at 1.0 V or below, a potential range far below those currently used for synthesis of ZrO_2 nanotubes. The formed film is made of amorphous ZrO_2 which shows the presence of nanopores and wire-like structures. These results contribute to expand the range of conditions to be considered in the future investigation of the synthesis of nanostructured zirconia films.

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