Effect of ethylene glycol on morphology of anodic alumina prepared in hard anodization

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A B S T R A C T

The influence of ethylene glycol (EG) on the morphology of anodic alumina fabricated during hard anodization (HA) was analyzed. A transformation from continuous nano-porous film to separated alumina nano-tubes was induced upon addition of EG to a 0.3 M oxalic acid solution. Moreover, while anodization under constant voltage in a 1:1 v/v EG:H_2O acidic solution resulted in distinct current density (i_a) reduction in reference with the i_a registered for the HA in an EG-free solution, the anodization in a 1:4 v/v EG:H_2O mixture was often accompanied by a sudden i_a increase and irregular current oscillations. In the latter case mostly the alumina nanotubes with wall thickness variation were produced. In general, the separation phenomena was explained by extensive incorporation of soluble $C_2O_4^{2-}$ and COO^- ions into the oxide framework leading to an enhanced oxide dissolution rate and preferred cleavages along the cell boundaries. The current oscillation and the production of nanotubes with an altered diameter were ascribed to a higher value of $\varepsilon_{el} \cdot \varepsilon_{ox} / \eta$ ratio (where ε_{el} and ε_{ox} are the dielectric coefficient of electrolyte and the formed anodic oxide, respectively, and η is the dynamic viscosity of the solvent) as compared to the value relevant for more viscous solvent.

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1. Introduction

Since it was first observed by Ono et al. [1,2] that high current density can be directly linked to high pore ordering, high field anodization was frequently applied as an effective way to produce a long-range ordered anodic alumina of various morphologies. Hard anodization (HA) was performed in oxalic [3–5], sulfuric [6,7], and phosphoric [8] acid solutions. Due to the application of high potentials new self-ordering regimes, in a wider range of the pore intervals, were found. A combination of mild and hard anodization allowed the fabrication of anodic alumina templates with alternating internal diameters and the template-assisted synthesis of periodically modulated nanostructures with novel magnetic properties [9–11].

Along with the self-ordering phenomena novel morphologies were occasionally observed in anodic alumina fabricated at high or ultra-high potentials. Two-step hard anodization conducted in a H_2SO_4–$Al_2(SO_4)_3$–H_2O mixture solution resulted in the formation of cells with several tiny pores in each cell [7]. Integrated alumina nanotubule arrays were observed after a process conducted at high field in sulfuric acid solutions [12,13]. Hard anodization under ultra-high potentials in an oxalic acid solution, using a constant-current non-linearly voltage increasing method, resulted in the production of nanotubes with a fluctuating thickness [14–16]. A combined anodization process in an ethanol–oxalic acid electrolyte made up of a voltage increasing process and constant current anodization led to the formation of fusiform alumina nanotubes [17].

Recently, it was noticed that geometrical features of porous anodic alumina (PAA) can be also affected by addition of various organic compounds to the acidic electrolyte solutions. It was found that the addition of ethanol can significantly increase the growth rate of PAA in a sulfuric acid solution [18]. Hard anodization performed in an ethanol modified oxalic acid solution resulted in larger pore intervals and a worse pore arrangement [19]. Opposite to that finding, the improved ordering of nanopores in PAA was observed in the ethylene glycol (EG) modified electrolytes [20,21]. The increasing PEG concentration decreased the growth rate of the PAA film at a given temperature [22]. Moreover, a decrease of the interpore distance [23] for a more viscous electrolyte was also observed. All these findings suggest that a modifier can play an important role in a PAA formation mechanism.

As demonstrated by Su et al. [24] the geometrical features of PAA, such as the pore size (D_p) to the interpore distance (D_{int}) ratio, are governed mainly by the dissociation rate of water. The dissociation rate enhances as the dielectric constant (ε) of a solvent decreases. It is well known that the ε of a water solution ($\varepsilon_{water} = 80.1$ at room temperature) can be reduced by the addition of a miscible organic solvent with a lower ε value [25,26]. Owing to the lower ε value, a gradual decrease of the current density upon an increasing amount of ethylene glycol (EG) in a sulfuric acid water solution ($\varepsilon_{ethylene\ glycol} = 37$ at RT) was observed [27]. Likewise, upon addition of ethanol ($\varepsilon_{ethanol} = 24.3$ at RT) a drop of i_a was registered [8,16,28]. When analyzing the influence of an additive on a PAA formation mechanism other parameters,

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such as the zeta potential and viscosity coefficient of a medium, need to be taken into account as well. Because ethanol is only slightly less viscous than water ($\eta_{ethanol} = 1.095$ mP s; $\eta_{water} = 0.89$ mP s at T ~ 27 °C), the lower current density is related rather with its ability to decrease the ε of an electrolyte and to decrease the temperature generated at the PAA barrier layer. However in the case of relatively viscous solvents such as EG ($\eta_{EG} = 16.2$ mP s at T ~ 27 °C), the influence of η on ion migration rate into the base PAA nanoholes cannot be neglected.

In this work, we analyze the influence of EG on the HA process in an oxalic acid solution and its impact on morphological features of the resulting anodic aluminum oxide (AAO). It was observed that the addition of EG leads to a radical change of AAO morphology from continuous nanoporous film to separated alumina nanotubes. The obtained results are opposite to the phenomena found during anodization of titanium, where upon the addition of an increasing amount of a viscous solvent with lower ε, the morphology of anodic titanium oxide (ATO) changes from separated nanotubular arrays to continuous oxide films [29–31]. As reported before, alumina cell separation phenomena can also occur during anodization under low current density in a glycolic acid solution [13] and in a 0.3 M oxalic acid EG solution [20]. On the other hand, the phenomena does not take place during mild anodization (MA) in an EG modulated sulfuric acid solution [27]. The previous findings and the results presented in this paper strongly suggest that the high electric field cannot fully elucidate the formation of the nanotubular morphology in AAO. Therefore, an alternative explanation is required to better understand the data. In this work, based on the analysis of the AAO produced in the EG-free and EG-modulated HA process it was suggested that that the alumina cell separation and nanotube formation arises from the low dielectric constant of bulk Al_2O_3 which is prone to increase in a medium with a higher ε. The increase of AAO's dielectric constant is due to both a high electric filed (E) and the incorporation of negatively charged ions (such as $C_2O_4^{2-}$ and COO^-) into the AAO framework. The effect enhances the alumina dissolution rate at the cell boundaries, thus leading to a cleavage between cells.

2. Experimental

High-purity aluminum foil (99.9995% Al, Puratronic, Alfa Aesar) with a thickness of about 0.25 mm was cut into coupons (2 cm × 1 cm). Before the anodization process the Al foils were degreased in acetone and ethanol and subsequently electropolished in a 1:4 mixture of 60% $HClO_4$ and ethanol at 0 °C, and a constant voltage of 20 V, for 2 min. Next, the samples were rinsed with ethanol and distilled water and dried. As prepared Al coupons were insulated at the back and the edges with acid resistant paint, and served as the anode. A Pt grid was used as the cathode and the distance between both electrodes was kept constant (ca. 5 cm). A large 1 l electrochemical cell, an electronic feed-back controlled bath with circulator, and vigorous stirring (750 rpm) were employed in order to maintain the low temperature required for the HA anodization. An adjustable DC power supply with a voltage range of 0–300 V and a current range of 0–5 A, purchased from NDN, model GEN750 TDK Lambda, was used to control the applied voltage, and APPA 207 TRUE RMS multimeters were used to measure and transfer the registered current and potential data to a computer.

The samples were prepared by a hard anodization (HA) method at voltages between 120 and 160 V in a 0.3 M $H_2C_2O_4$ water-based solution and in EG-modulated solutions with 4:1 v/v water to EG and 1:1 v/v water to EG mixtures, at 0 °C. Prior to application of a given voltage, the samples were pre-anodized at 40 V for 5–8 min. Then, the voltage was slowly increased to a target value at the rate ranging from around 0.04 to 0.06 V/s, and the samples were anodized for 2 h. As obtained, alumina was chemically removed in a mixture of 6 wt.% phosphoric acid and 1.8 wt.% chromic acid at 60 °C for 120 min.

Morphology of PAAs was studied using field-emission scanning electron microscope FE-SEM (FEI, Quanta) equipped with energy dispersive X-ray spectrometer (EDS). The chemical composition analysis

was performed at 20 kV, magnification of 1000, and with a constant distance of samples to the detector. Each measurement was repeated three times and an average of the three measurements was taken to determine the chemical composition of a studied sample.

To obtain geometrical parameters of the fabricated Al nanoconcaves, Fast Fourier transforms (FFTs) were generated based on three SEM images taken at the same magnification for every anodizing voltage, and were further used in calculations with WSxM software [32]. The average interpore distance (D_c) was estimated as an inverse of the FFT's radial average abscissa from three FE-SEM images for each sample. To estimate regularity ratio, radial average was generated from each FFT image. The regularity ratio (RR) was calculated according to the following formula (Eq. (1)) [33]:

$$RR = \frac{H}{W_{1/2}} \cdot \frac{\sqrt{n}}{S^{3/2}} \tag{1}$$

where n is the number of pores, S is the analyzed surface area, H is the maximal intensity value of the FFT intensity profile, and $W_{1/2}$ is the width of the intensity profile at half of its height.

3. Results and discussion

In Fig. 1a–c the current density/voltage vs. time curves measured for HA performed in a water-based oxalic acid solution and in the electrolytes with two different EG–water mixtures are presented. In general, the HA method consists of two stages: anodization under the increasing voltage and a stable-voltage anodization. Voltage increase up to a target value is followed by the increase of the current density (i_a). Despite the fact that the effect of the anodization voltage ramp on the pore arrangement was proven to be negligible in contrast to the hard anodization voltage effect [34], small differences in the voltage ramp (~0.04–0.06 V/s) can be still reflected in the i_a-time transients. However, independent of the insignificant influence of various voltage ramps on the current course, some characteristic points in the i_a-time curves can be distinguished. In the curves registered for anodization performed in the electrolyte without EG (Fig. 1a) the i_a grows with potential until ~80 V. Between 80 and 130 V, despite a continuous voltage increase, the i_a starts to decay. Finally, above 130 V the current rises abruptly. As an effect, in the i_a-time transients two distinct peaks can be distinguished. In some i_a-time curves acquired during HA in an electrolyte with a 4:1 v/v water to EG mixture (Fig. 1b) there are more than one sensitive voltages above which a sudden drop or rise of i_a can be observed. Consequently, sometimes more than two peaks can be discriminated. In the current course registered for HA in an oxalic acid solution with 1:1 v/v water/EG mixtures (Fig. 1c) the peaks generated by the sensitive voltages become almost invisible, and as a result, generally only one peak is discernible. After reaching a target voltage, the HA process proceeds to the second stage. During the stable-voltage anodization the current density decreases exponentially owing to limited diffusion of the ionic species (e.g., $C_2O_4^{2-}$) from the electrolyte to the electrolyte–oxide interface. This happens for all the analyzed samples except for the ones anodized at 130, 140, and 150 V in a 4:1 v/v H_2O/EG mixture. In the latter case, the current decrease is more gentle and the i_a begins to fluctuate chaotically. A similar current fluctuation was previously registered for anodization conducted at ultra-high potentials [15,16]. The unstable current oscillation was also observed in the anodization performed in a concentrated pyrophosphoric acid solution, which resulted in the formation of anodic alumina nanofibers [35,36]. The i_a oscillation is absent or is suppressed to a level below the resolution of the current measurements in the samples anodized at 120 and 160 V. The lack of i_a fluctuation at 120 V is probably due to the relatively low potential. However, a totally different shape of the i_a curve acquired for the sample anodized at 160 V is quite surprising and may be linked with a more gentle current rising at the increasing voltage stage (Fig. 1 b). The difference in the current course may also come from the quality