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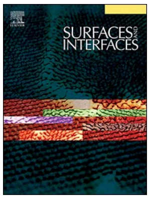

Surface characterization of nanoporous aluminium oxide films synthesized by single-step DC and AC anodization

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ABSTRACT

Nanoporous alumina films were synthesized on commercial grade aluminum substrates using single-step anodization technique in 0.3 M phosphoric acid at room temperature. Effect of applied voltage (100–130 V) on surface characteristics of anodized aluminum oxide (AAO) film was investigated. Surface topography parameters and regularity ratio of nanopores arrangement were characterized using power spectral density (PSD) and fast Fourier transform (FFT) profiles. While DC anodization suffered from filament-like cavities at 130 V owing to thermally enhanced dissolution of oxide, AC anodization produced localized flower-like morphology for all the applied voltages. The intensity of localized flower-like morphology was increased monotonically with applied voltage. Evolution of flower-like morphology was discussed on the basis of Pashchanka-Schneider model.

1. Introduction

Nanoporous anodic aluminum oxide (AAO) has a tremendous potential in large spectrum of nano-scale engineering applications ranging from template-assisted synthesis of nanowires to MEMS/NEMS based tribology devices [1–4]. Numerous efforts have been made in the literature to understand the mechanism of pattern formation during aluminum anodization [5–10]. The field-assisted dissolution model [5–9] suggests that oxide film growth occurs at the metal/oxide interface owing to inward migration of O^{2-} ions across the barrier layer and the pores are formed mainly at the oxide/electrolyte interface due to electric field-accelerated dissolution of anodic alumina accompanied by outward migration of Al^{3+} ions into the electrolyte. The stress-driven viscous flow model [10–12] claims that nanopores are generated mainly by flow of material from the pore bases to the cell walls and this material displacement is primarily facilitated by plasticity of the oxide film. The oxygen bubble model [13–15] emphasizes that the evolution of O_2 occurs with the formation of oxide film, and whether or not this oxide film has been transformed from barrier type to porous type, can be determined by observing whether or not O_2 separates out of the bulk oxide film. Later, Pashchanka et al [16–18] proposed the novel theoretical model for nanoporous pattern formation by adopting the analogy of Rayleigh-Bernard convection cells. While the temperature gradient is the driving for Rayleigh-Bernard convection cells, the applied voltage is considered as a driving force for pattern formation in porous oxide film [16]. However, it is very difficult to provide the unified theory describing all the aspects of random experimental observations during aluminum anodization. Nevertheless, Pashchanka-Schneider model describes the wide range of unexplained experimental observations for the formation of equal-sized hexagonally ordered pores [16].

The self-ordering of nanopores in anodized aluminium oxide (AAO) film is governed by several anodization parameters such as applied voltage [19], time [20], temperatures [20] and pH [21], concentration [21], conductivity, viscosity [22] and composition [23] of the applied electrolyte. Pashchanka et al [16] proposed an empirical relationship between these anodization parameters as follows:

$$P = \frac{Q_{av}\Delta U}{\eta} = \frac{10^{-pH}\Delta U}{C\eta} \tag{1}$$

Where P is the porosity number or criterion for the appearance of self-organized nanopores (found experimentally to be around 0.057 for the majority of the widely used electrolytes), Q_{av} is the average charge of supporting electrolyte anions, 10^{-pH} is the proton concentration, ΔU is the applied voltage, η is the dynamic viscosity, σ is the specific electrical conductivity and C is the acid concentration. The Eq. (1) demonstrates that the self-ordering voltage mainly depends upon the applied electrolyte. For instance, the lower voltages (15–30 V) are preferred for the less viscous solutions of sulfuric acid and oxalic acid while the higher voltages (160–195 V) for a viscous phosphoric acid

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[16]. Stepniowski et al [20] investigated the influence of time and temperature on the arrangement of alumina nanopores. They observed that the better ordering of alumina nanopores occurs in second-step anodization if first-step anodization is performed for longer duration owing to better pre-texturing of the aluminum beneath the pore bottoms, at the metal–oxide interface and the applied temperature has no effect on ordering of nanopores for a short time anodization. Stepniowski et al [21] mentioned that interpore distance between nanopores linearly scales with applied voltage while it increases exponentially with molar fraction of chromic acid electrolyte.

Most researchers synthesized self-organized nanoporous aluminum oxide films by utilizing the combination of high purity aluminum substrate and low temperatures (0-10 °C) by using DC anodization [24–27]. This combination is generally preferred as the existence of any chemical impurities shall not allow sustainable growth of oxide film owing to thermally enhanced dissolution and dielectric breakdown [28] at the metal-oxide interface during DC anodization. However, there has been significant interest among the aluminum industry for alternating current (AC) and pulsed current anodization to fabricate nanoporous AAO films on commercial grade Al-alloys and low purity aluminum substrates under ambient environment [29–33]. De Graeve et al [29] investigated the contribution of cathodic process during AC anodization of commercial Al-alloys, and observed that cathodic hydrogen gas evolution develops high cathodic potential at flaw sites tending to reduce the efficiency of film formation. In recent years, pulsed current techniques seem to be gaining attraction since it overcomes most of the disadvantages (thermally enhanced dissolution of DC anodized film, limited thickness, and inferiority in the quality of AC anodized film) associated with conventional DC and AC anodization techniques. Lee et al [31] proposed pulse anodization approach that combines the advantages of mild anodization (formation of self-ordered nanopores) and hard anodization (high production rate). Law et al [32] tailored the optical properties of AAO photonic crystals by controlling the various anodization parameters precisely using sawtooth-like pulse anodization. Chung et al [33,34] proposed the novel hybrid pulse anodization technique to synthesize AAO films on commercial grade purity Al substrates (99%) at room temperature condition itself. The basic idea behind this hybrid pulse approach was to suppress any temperature rise by facilitating the cooling of electrolyte during the pulse-off period. The incorporation of cathodic cycle using alternating current may reduce the dissolution tendency of oxide layer at impurity sites to the certain extent. It is noted that certain engineering applications such as hydrogen gas storage [35,36], catalysis [37,38], electrochemical sensing [39] , membrane synthesis [40,41] and corrosion protection coatings [21,42,43] shall not need any self-organized or well-ordered nanopores. Moreover, AC anodization has distinct practical advantages relative to DC anodization. For instance, it is possible to obtain anodization for two different aluminum substrates at the same time during AC anodization. AC anodization also minimizes the necessity for pretreatment of the aluminum substrates and agitation of anodizing electrolyte owing to hydrogen gas evolution during cathodic cycle. In fact, AC anodization can be considered as one of the simplest, economic and affordable industrial techniques in the mass production of corrosion protection coatings for large-scale aluminum sheet and food packaging applications [29]. Despite the mechanism of nanoporous oxide formation during AC anodization is similar to that of DC anodization; the characteristics of film morphology, surface topography and regularity ratio of poorly arranged nanopores may be varied as a function of applied voltage during AC and DC anodization. Furthermore, the nature of film morphology and surface topography play decisive role in determining the mechanical and frictional behavior of AAO films for surface engineering related applications [44–46]. Main objective of the present study was to understand the evolution of film morphology, surface topography and regularity ratio of poorly arranged alumina nanopores obtained on commercial grade Al substrates by varying applied voltage (100–130 V) using single-step DC and AC anodization.

2. Experimental methods

Commercial grade Al substrates of 99.0% purity were utilized to fabricate nanoporous aluminium oxide films by single-step anodization. Firstly, the surface area of Al specimens (15 mm x 15 mm x 0.25 mm) was coated with an insulative polymer film after leaving an exposed area of 1 cm^2 for anodization process. Al specimens were then subjected to chemical polishing in 1 M solution of NaOH for two min in order to achieve the mirror-like surface finish. Subsequently, single-step D.C. and A.C. anodization were performed on these polished Al substrates in 0.3 M phosphoric acid solution at a constant applied voltage of 100, 110, 120 and 130 V for 15 min. DC-current was supplied from DC power source (Zeal-Tech instrument, Model No.9211, India) while AC-current was supplied from single phase auto transformer (Crown Instrument, Model No.C10ASPT, India). All the anodization experiments were performed at room temperature (30–35 °C) and water bath was used as a heat sinking source during anodization. The presence of thin whitish gray layer on Al substrates confirmed the formation of AAO films. Three specimens were prepared for each set of process parameters to ensure repeatability in the experimental data. It should be kept in mind that single-step anodization results in the formation of poorly arranged nanopores, unlike two-step anodization which leads to the formation of well-ordered hexagonal nanopores. Surface characteristics of AAO films fabricated on commercial grade aluminum substrates were analyzed by scanning electron microscope (SEM, JEOL JSM-6610LV, Japan), and atomic force microscope (AFM, Bruker Multimode 8, USA) respectively. Power spectral density (PSD) and Fast Fourier transforms (FFT) profiles were derived from AFM images and SEM micrographs in order to evaluate the surface topography parameters and regularity ratio of pore arrangement for all the AAO films, synthesized at various D.C. and A.C. voltages.

3. Results and discussion

Fig. 1 depicts the variation of current as a function of time for both AC and DC anodization. In typical AC anodization, the aluminum specimen serves as an anode for every 0.01 s (at a given frequency of 50 Hz) and for the same consecutive period, it acts as a cathode due to polarity shift in the voltage. However, aluminum remains as anodic material during the entire period for the case of DC anodization. Fig. 2 shows the SEM micrographs which represent the evolution of surface morphology of anodized specimens performed by DC and AC anodization techniques. It is evident that the nature of surface morphology is more or less appeared to be similar at 100 V (compare Fig. 2(a) and

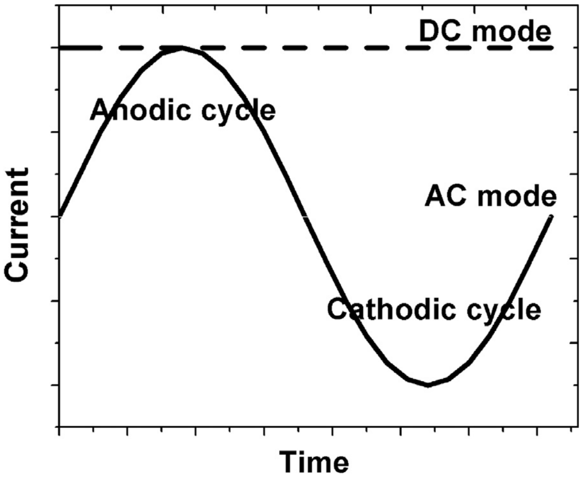

Fig. 1. Variation of current as a function of time for DC and AC anodization process.