



Influence of anodization parameters on the volume expansion of anodic aluminum oxide formed in mixed solution of phosphoric and oxalic acids



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ABSTRACT

The growth of anodic alumina oxide was conducted in the mixed solution of phosphoric and oxalic acids. The influence of anodizing voltage, electrolyte temperature, and concentration of phosphoric and oxalic acids on the volume expansion of anodic aluminum oxide has been investigated. Either anodizing parameter is chosen to its full extent of range that allows the anodization process to be conducted without electric breakdown and to explore the highest possible volume expansion factor. The volume expansion factors were found to vary between 1.25 and 1.9 depending on the anodizing parameters. The variation is explained in connection with electric field, ion transport number, temperature effect, concentration, and activity of acids. The formation of anodic porous alumina at anodizing voltage 160 V in 1.1 M phosphoric acid mixed with 0.14 M oxalic acid at 2 °C showed the peak volume expansion factor of 1.9 and the corresponding moderate growth rate of 168 nm/min.

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1. Introduction

Over the past century, aluminum oxide with prominent features of large band gap, barrier height, dielectric constant, good adhesion, mechanical strength, thermal stability, and corrosion resistance is one of the most favorable ceramic that has been investigated and used in both laboratories and industries [1–3].

The thickness, interpore distance, and diameter of self-ordering pore arrays of anodic aluminum oxide (AAO), to which have been paid great attention for the applications in nanostructures, are the most commonly used parameters to define the AAO membrane. On the other hand, the volume expansion factor is another important parameter as the indicator of how efficient is the growth of AAO and close related to the efficiency of anodizing current density. The volume expansion factor is the ratio of the volume of the AAO formed to the volume of Al consumed, and simplified to the thickness ratio of AAO formed to Al consumed [4–7].

Recently, the effects of current density and temperature on volume expansion factor, and efficiency of porous alumina formed in sulphuric and oxalic acids were investigated [8,9]. The factor was reported to have linear dependence on the logarithm of the anodizing current density at a particular temperature and decreases with

the increase in the electrolyte temperature at a given current [8,9].

The formation mechanisms of AAO in acid at aluminum/oxide and oxide/electrolyte interfaces were proposed [10–14]. The anodizing voltage and acid activity were related to barrier-layer thickness and pore diameter, and the mechanism of field-assisted dissolution was also established [10]. The majority of AAO is formed at aluminum/oxide interface due to higher ion transport number of O^{2-} and OH^{-1} than Al^{3+} , which formed at the oxide/electrolyte interface also favors the Al^{3+} transfer into the electrolyte [11,12]. A tungsten tracer was used to reveal the details of mass transport within PAA films, and a flow model was established to explain the motion of the AAO and the formation of pores [15,16].

From the previous finding, it is known that the volume expansion factor can be very dependent on the anodization conditions, which determine the electric field, local temperature, and ion transport, thus the rates of both aluminum consumed and AAO formed. Typically, the reported volume expansion factors, anodized in acids, were determined to be in the range of 1.25–1.7 [4–6,9,17–19], which value is approximately between the calculated of factors for AAO of 2.1 for $Al(OH)_3$ and 1.29 for $\alpha-Al_2O_3$ with assumption of 10% porosity and 90% current efficiency [7,17–20]. On the other hand, the reported volume expansion factors were mainly determined for a limited set of anodizing conditions, which is crucial as anodic oxidation dynamics of aluminum in acid change with the high anodizing voltage and activity of acid.

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To the best of our knowledge, this is the first to report the influence of anodization parameters on volume expansion factors of anodic aluminum oxide formed in mixed solution of phosphoric and oxalic acids, which factors show an initially increase till the vertex then a drop dramatically with further increase in either of the parameters with other fixed.

2. Experimental details

2.1. Preparation of samples

The aluminum foil (99.98% purity) used in the electrolytic capacitors was adopted as the anodized material. Prior to anodizing, the aluminum foil was electropolished in a mixture of H_3PO_4 , H_2SO_4 , and deionized (DI) water with ratio of 2:1.8:1 by weight under constant current of 2 mA at 75 °C for 7 min. Both surfaces of sample are protected by tapes after electropolishing except the central area of 1.2 cm² on one side of sample, which will be exposed to electrolyte.

2.2. Anodization

The anodizing process was conducted in a two-electrode temperature-controlled cell with a graphite cathode. A Keithley 2400 source meter was used as the power supply for the electrochemical process under constant cell potential. The exposed area of the sample was submerged into the temperature-controlled electrolyte and not attached to a heat sink.

The anodizing parameters dependence of volume expansion factor of AAO growth is examined through the change of anodizing voltage, concentration of phosphoric acid, addition of oxalic acid, and temperature from 110 to 160 V, 0.5 to 2.0 M, 0 to 0.185 M, and 0 to 7 °C, respectively. Either anodizing parameter is chosen to its full extent of range that allows the anodization process to be conducted without electric breakdown and to explore the highest possible volume expansion factor.

From our previous work [21], a mixed aqueous solution of oxalic acid and phosphoric acid can result in a better circular symmetry and more uniform diameter of the pore opening of alumina. Therefore, the additional amounts, 0, 0.07, 0.14, and 0.185 M, of oxalic acid were mixed with 1.1 M phosphoric acid to serve as the anodizing electrolyte. The anodization conditions, variation range of anodizing parameter and corresponding pH values of electrolytes are listed in Table 1.

The aluminum consumed after anodizing growth was obtained by measurement of the step height between protected aluminum surface and bottom surface of porous alumina with alumina removed at the edge of anodized area with α -step profiler. The thickness of AAO formed was obtained by SEM cross section image. For qualitative description of the influence of anodization parameters on the volume expansion of aluminum, the porosity was not taken into account in the calculation of volume expansion factor.

3. Results and discussion

3.1. Influence of anodizing voltage

The anodizing voltage dependence of volume expansion factor and growth rate for AAO formed in 1.1 M phosphoric acid at 2 °C is shown in Fig. 1(a) and (b), shows the corresponding current density, thickness of aluminum consumed and AAO formed versus anodizing voltage.

As can be seen from Fig. 1(a), the initial linear dependence of volume expansion factor of aluminum anodized in 1.1 M phosphoric acid on the anodizing voltage continues till its peak value at about 160 V, and then quickly decreases with the anodizing

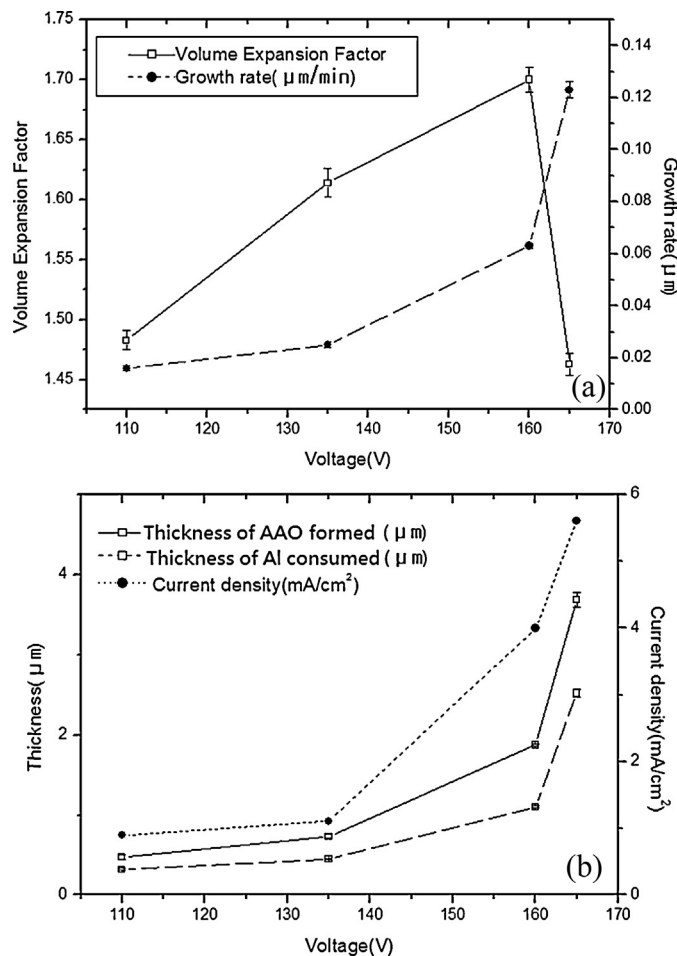


Fig. 1. Anodization of an aluminum foil in 10% phosphoric acid at 2 °C: (a) volume expansion factor and AAO growth rate versus anodizing voltage; (b) anodizing current density, thickness of AAO formed and thickness of Al consumed versus anodizing voltage.

voltage. However, the growth rate of aluminum oxide still keeps up with the increase in the anodizing voltage.

On the surface the thickness of AAO formed and aluminum consumed may be proportional to the anodizing current density according to the Faraday law. Conversely, it is observed from the Fig. 1(b) that neither thickness of AAO formed nor aluminum consumed vary proportional to the anodizing current density. Nevertheless, the increasing patterns of the thickness of AAO formed and aluminum consumed versus anodizing voltage are similar to that of anodizing current density versus anodizing voltage.

The deviation from proportional relationship between the thickness of aluminum consumed and anodizing current density implies that the Al^{3+} ion transport number within oxide plays an important role. In addition, the electron leakage current due to the local states created within the forbidden band gap by the incorporation of conjugate anion of acids into the outer oxide layer [22] is suggested to contribute part of the anodizing current beside the O^{2-} and Al^{3+} ions.

The deviation from proportional relationship between the thickness of AAO formed and anodizing current density suggests that the electric-field assisted ejection of Al^{3+} ion and/or dissolution at interface of oxide/electrolyte plays the additional key roles. Therefore, anodizing current density, thickness of aluminum consumed, and AAO formed are not necessary proportional to each other, which result the nonlinear nature of volume expansion factor.

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