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Stability of nanopore formation in aluminum anodization in oxalic acid

LI Xian-feng, CHEN Dong, CHEN Zhe, WU Yi, WANG Ming-liang,
MA Nai-heng, WANG Hao-wei

State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering,
Shanghai Jiao Tong University, Shanghai 200240, China

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Abstract: The effect of applied voltage on nanopore formation stability of porous anodized alumina (PAA) in oxalic acid electrolyte was investigated. The Al anodization at a constant applied voltage is a popular electrochemical method to synthesize PAA templates. The experimental observations of Al anodization are used to compare the predictions of the THAMIDA model for interpore distance and the stability criterion of the SINGH model. It is found that, in the electrolyte of pH = 0.96, the interpore distance—applied voltage has a linear dependence coefficient of 2.24 nm/V, which agrees well with the THAMIDA model. It has also been confirmed that pore formation is instable at above 60 V which can be predicted by SINGH model. A second unstable growth regime below 30 V is also observed, which is not predicted by any of the models.

Key words: aluminum anodization; porous anodized alumina template; electrochemical synthesis; porous membrane; nanomaterial

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1 Introduction

Porous anodized alumina (PAA) membranes have been used intensively to synthesize nanowire and nanotube arrays. These membranes offer nanochannels of high regularity and high diameter-to-length aspect ratios through their thicknesses [1−3]. PAA membranes can be fabricated by electrochemical anodization of pure aluminum in a variety of electrolyte solutions [4−6]. KELLER et al [7] first reported the creation of nanopore arrays grown perpendicularly to the aluminum surface with relatively low regularity. MASUDA and FUKUDA [8] demonstrated that highly ordered nanopore arrays can be obtained by a two-step anodization method from high purity (99.999%) aluminum. Since then, PAA templates have been widely used as host materials for nanomaterials fabrication.

Although a large amount of work has been done on the PAA template fabrication, understanding of the mechanism of pore formation in PAA templates is yet to be established. Several theoretical models have been suggested in Refs. [9−13] to explain the pore formation process, but there is generally lack of systematic experimental verification of these models.

THAMIDA and CHANG [10] proposed a model to predict the pore growth stability based on the concept of electric field enhanced dissolution of Al_2O_3. They also predicted the dependence of interpore distance (D_{int}) to applied voltage (V) and electrolyte concentration (pH value, V_{pH}) as:

$$D_{\text{int}} = \frac{2.96V}{2.31 - 1.19V_{\text{pH}}} \tag{1}$$

Equation (1) is valid for pH < 1.3. For 1.3<pH<1.77, the interface dissolution rate becomes so small that the mathematical approximation of the exponential rates in the derivation is invalid for the equation. For pH > 1.77, pores do not form due to a very thick barrier layer. Further, they defined the concept of two-dimensional stability with well ordered pores and uniform size. Based on the THAMIDA model, SINGH et al [11] analyzed the mechanisms on the pore initiation and suggested that there existed a critical voltage when the unstable pore growth occurred.

FRIEDMAN et al [14] carried out a systematic experimental investigation to verify the THAMIDA model and the SINGH prediction. Their experimental observations did not agree with either the THAMIDA model or the SINGH model. However, their experiments [10] were mostly performed at pH≥1.28 (oxalic acid) and pH=1.57 (phosphoric acid), which are close to the limits

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Corresponding author: WANG Ming-liang; Tel: +86-21-54747597; Fax: +86-21-54747597; E-mail: mingliang_wang@sjtu.edu.cn

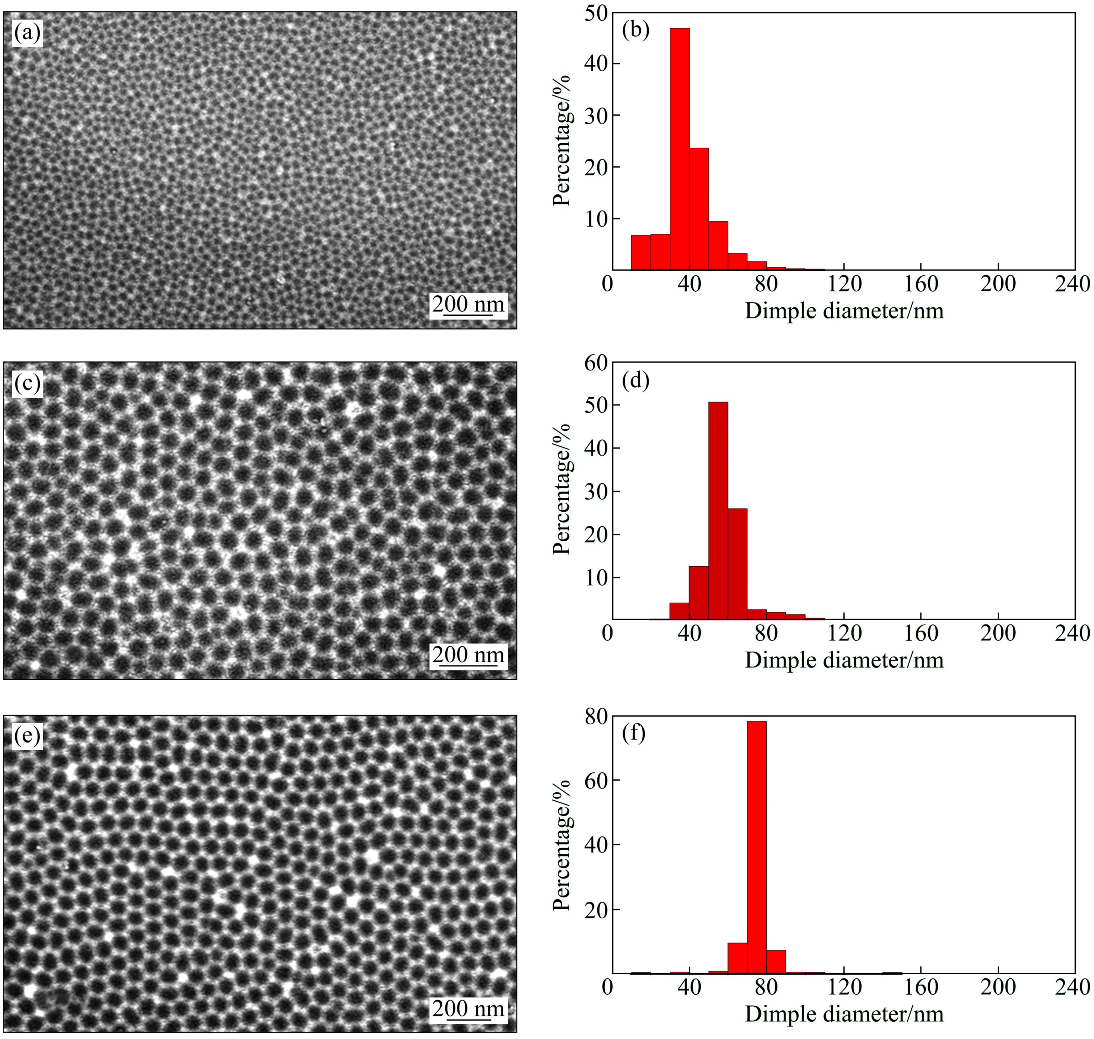
for the validity of Eq. (1). The stability results for both oxalic acid and phosphoric acid were on the contrary to the SINGH prediction in the low and medium applied voltages ranges, and complied with the theory in the high voltage range. This work attempts to verify the predictions of these two models on dimple structures from the first anodization in oxalic acid electrolyte.

2 Experimental

The electrochemical anodization was performed on pure Al (99.999% purity) plate in 3% (mass fraction) oxalic acid (pH=0.98) electrolyte. A titanium plate was used as the cathode. The distance between the two electrodes was 660 mm. A series of samples were anodized under different bias voltages ranging from 20 V to 70 V for 2 h. The alumina layer formed was etched away in a solution containing 18 g/L chromic acid and 60 g/L phosphoric acid at 80 °C for 1 h. The dimpled surface of the etched samples was examined using a Zeiss 1555 field emission scanning electron microscope (FESEM). The average dimple diameter and inter-dimple spacing were determined by analyzing the SEM micrographs using Image J software.

3 Results and discussion

Figure 1 shows SEM images of the dimple structures of eight samples anodized under different voltages. The graphs in the right column show the dimple size distribution of the images to their left. The scale bars in all the images are 200 nm. It can be seen that the samples fabricated at 20 V and 30 V show relatively narrow pore size distribution, but the pore pattern is less than well organized as in the samples anodized at higher voltages. These samples are considered of unstable growth. The samples prepared at 40, 45 and 50 V show well ordered pore structures in hexagonal arrangement and narrow size distributions. The pore formation in these samples is stablie during anodization. The samples fabricated at 60, 65 and 70 V show obviously less ordered arrangement of the pores with broader size distributions. These samples have undergone unstable growth. The pore structures of these samples conform to typical KURAMOTO-SIVASHINSKY phenomenon, with monotonic instability



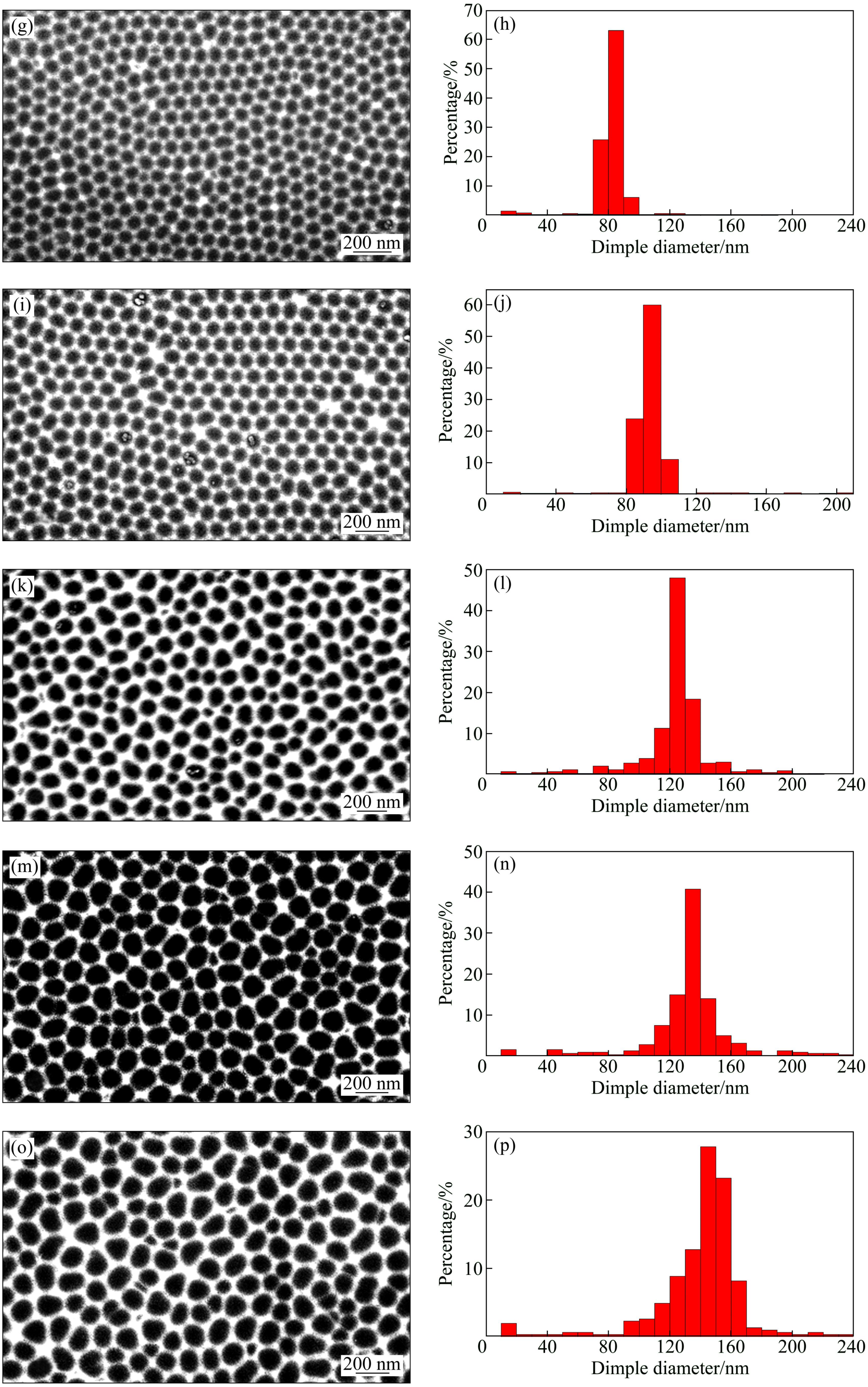


Fig. 1 Dimple structures after first anodization performed at different bias voltages and corresponding size distribution of pores: (a,b) 20 V; (c,d) 30 V; (e,f) 40 V; (g,h) 45 V; (i,j) 50 V; (k,l) 60 V; (m,n) 65 V; (o,p) 70 V

in the long-range and spatiotemporally chaotic cells, splitting and merging, in the short range, but having a well-defined average pore size [11].

Figure 2 shows the mean dimple diameter as a function of the voltage applied. The upper and lower limits of the error bars in the figure represent the 5% and 95% statistical values of the distribution. It can be seen that the mean dimple diameter increased linearly with the voltage with a coefficient of 2.08 nm/V. The dimple size distribution range remained low up to 50 V and then increased significantly at higher voltage levels, indicating unstable growth. It is also noticed that there is a moderate increase in the range width with decreasing the voltage to below 30 V. This demonstrates another regime of low growth stability at the low voltages. The SINGH theory predicts only one unstable growth region at high voltages. The experiment results obeyed the SINGH theory well with the exception of the unstable growth at below 30 V.

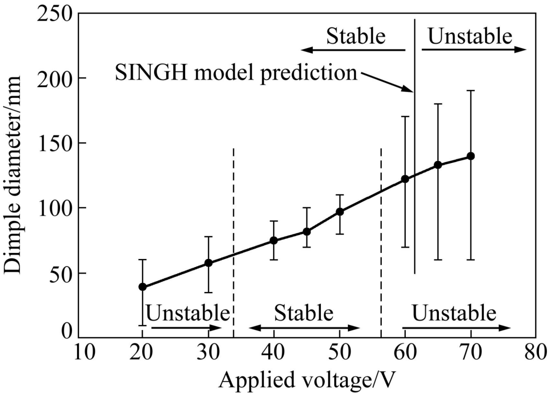


Fig. 2 Effect of applied voltage on average dimple diameter (Error bars indicate 5%−95% distribution boundaries)

Figure 3 shows inter-dimple spacing as a function of the applied voltage for anodization in 3% (mass fraction) oxalic acid solution with pH=0.96. The inter-dimple distance exhibited a linear dependence on the applied voltage within the range presented, with a coefficient of 2.24 nm/V. The straight line represents the prediction of the THAMIDA model, as expressed in Eq. (1). The linear dependence coefficient for Eq. (1) is 2.54 (pH=0.96), which agrees well with the experimental results.

The linear relationship between interpore distance and the applied voltage has also been experimentally identified in several previous studies [9,15]. LEE et al [16] found a linear correlation coefficient of 2.5 nm/V irrespective of acids used in the anodization, based on experimental observations from different studies. The acids collected in their analysis include 3% (mass fraction) (0.3 mol/L) H_2SO_4 [15], 17% (10%, volume fraction) H_2SO_4 [17], 2.7% (0.3 mol/L) $H_2C_2O_4$ [18], 10% H_3PO_4 [15], 1% (0.1 mol/L) H_3PO_4 [5]. This implies the generality of the THAMIDA model expressed in Eq. (1).

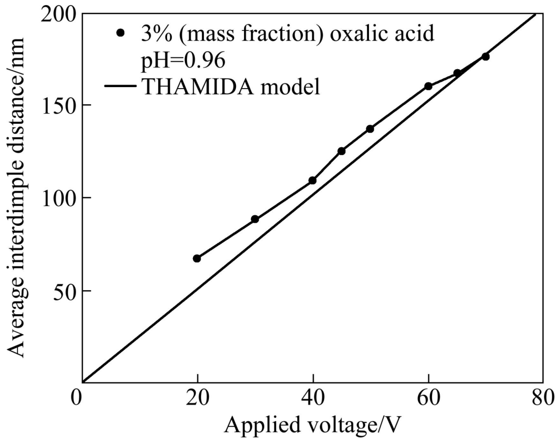


Fig. 3 Effect of applied voltage on inter-dimple distance for one step anodization compared to prediction of THAMIDA model for oxalic acid with pH=0.96

4 Conclusions

1) Dimple arrangement and size distribution are found to agree with the predictions of the SINGH model, with a threshold voltage for unstable pore growth of 60 V in 3% (mass fraction) oxalic acid solution (pH=0.96).

2) Unstable growth happens at lower voltages, below 30 V, which is not predicted by the SINGH model. The coefficient of the linear dependence of interpore spacing on applied voltage is determined to be 2.24 nm/V, which agrees with the THAMIDE model.

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草酸中阳极氧化铝纳米孔洞形成的稳定性

李险峰，陈东，陈哲，吴一，汪明亮，马乃恒，王浩伟

上海交通 大学材料科学与工程学院，金属基复合材料国家重点实验室，上海 200240

摘 要：研究在金属铝阳极氧化过程中外加电压对于纳米阳极氧化铝孔洞形成稳定性的影响。恒定外加电压下的金属铝阳极氧化是制备纳米孔洞阳极氧化铝材料的常用方法。金属铝阳极氧化的实验结果分析主要基于 THAMIDA 模型和 SINGH 模型。经分析发现：在 pH=0.96 的草酸溶液中进行阳极氧化，纳米氧化铝的孔间距与外加电压之间呈线性关系(2.24 nm/V)。此实验规律与 THAMIDA 模型的预测完全符合。另一方面，氧化铝纳米孔在 60 V 电压以上不稳定形成。SINGH 模型能预测此失稳区域的存在。此外，在低电压下(≤30 V)阳极氧化铝孔洞亦呈现不稳定形成。但是，现有理论没有预测这类失稳区域的存在。

关键词：阳极氧化；多空氧化铝模板；电化学合成；多孔模；纳米材料

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