Article ID: 1003-6326(2003)02-0298-04

Fabrication of anodized aluminum oxide membrane with nanometer pores①

ZHANG Zheng-fu(张正富), YANG Xian-wan(杨显万), ZHAO Yun-cheng(赵云臣),
CHEN Qing-hua(陈庆华), SUN Jun-sai(孙俊赛)
(Faculty of Material and Metallurgy Engineering,
Kunming University of Science and Technology, Kunming 650093, China)

Abstract: The pure aluminum and Al-Mg-Mn alloy were anodized in 4%, 10% and 18.5% phosphoric acid solution, respectively. As for pure Al, the maximum thickness of anodized aluminum oxide (AAO) membrane, 216 nm, is obtained by being anodized in 4% solution. Its average pore diameter is around 70 nm, and pore density exceeds $10^{10}/cm^2$. Under the same technology condition, the membrane thickness decreases with increment of electrolyte content. TEM images show that element Mg or Mn added into aluminum alloy can damage the integration of AAO membrane. During anodizing of aluminum, the formed oxide layer is amorphous. After being annealed at 600 ℃ for 24 h, it is still amorphous. However, when membrane is annealed at 930 ℃, the amorphous oxide begins to transform to γ-Al_2O_3.

Key words: anodized aluminum oxide; nanopore; phosphoric acid; membrane; alloying element; annealing

CLC number: TG 174 **Document code:** A

1 INTRODUCTION

Porous anodic film on aluminum is commonly formed by anodic oxidation of the aluminum substrate in acidic electrolytes, e.g. sulfuric, phosphoric, and oxalic acid solutions. The film is applied for various purposes, including the enhancement of the corrosion or abrasion resistance of the aluminum substrate, or as the pretreatment for subsequent processing such as painting or bonding[1]. Recently, anodized aluminum oxide (AAO) membrane is also employed in several new areas, for example, precise filter[2], gas sensor[3], optical-electronics devices[4-6], templates for synthesizing nanostructure[7-15].

Especially, assembly ordered nanostructures show many unique physic and chemical properties, e.g. macro-quantum tunnel effect, quantum size effect, Coulomb blockade effect, and so on[16]. These effects have opened up numerous possibilities for developing new electronic or optical devices. In general, ordered nanostructure can be fabricated with many technologies, e.g. electron/ion beam lithograph[17, 18], self-assembly[19-23], underpotential electrodeposition[24] and template assistant synthesis[7-15]. Template synthesis is more economical than other methods and suitable for preparing scaled-up materials. Many templates were used for this aim, and some of them have well arranged periodic or quasi-periodic structure, for example, porous AAO membrane[7-15], atom face in single crystal[24], macromolecule self-organized film[25] and so on.

There is a nano-sized pore array arranged quasi-periodically in AAO membrane. The diameter, center-to-center spacing between the pores and length of the pores can be easily controlled by varying the electrochemical parameters[26]. So, AAO membranes have been used extensively for synthesizing ordered nanometer materials[7-15]. In order to fit for various synthesizing conditions and usage purpose, the thickness and the phase constituent of AAO membrane, and the integration of the pore array are important properties. In this study, the dependence of membrane thickness on technology, influence of aluminum purity on integration of the pore array and heat-treatment on phase constituent of membrane are studied.

2 EXPERIMENTAL

The starting materials, 99.999% pure Al foil and LF_2 aluminum alloy (Al-Mg-Mn alloy, Mg 2.5%, Mn 0.2%), were degreased in acetone, then electropolished in perchloric acid + ethanol solution (20 mL perchloric acid + 80 mL ethanol) at 25 ℃ under a voltage of 20 V for 10 min. The foils were then DC anodized in acidic solutions to form a layer of

① **Foundation item:** Project(50161002) supported by the National Natural Science Foundation of China; Project(2001E0007Q) supported by the Natural Science Foundation of Yunnan Province, China; Project supported by the Postdoctoral Fund of Ministry of Personnel, China

Received date: 2002-09-26; **Accepted date:** 2002-12-27

Correspondence: Dr. ZHANG Zheng-fu, E-mail: ylzzf@sohu.com

porous alumina. In this study, all the samples were anodized in phosphoric acid solution under a constant voltage of 40 V, using a lead cathode. The anodized aluminum foil was immersed into saturated $HgCl_2$ solution. Hg^{2+} ions were reduced to mercury by aluminum. At the same time, AAO membrane was separated gradually from foil with aluminum solving into mercury. Some membranes were annealed at elevated temperature in air.

The microstructure of membrane was investigated with transmission electron microscope (TEM) (Philips EM420). The crystal structure of membrane was checked by X-ray diffractometry (Rigaku D/MAX-2000). The thickness of AAO membrane was measured on the basis of interference principle with JCD3 optical microscopy with light wavelength of 589.3 nm.

3 RESULTS AND DISCUSSION

Fig. 1 shows the dependence of membrane thickness on the content of phosphoric acid solution and anodizing time for pure aluminum. In 4% solution, the thickness increases with anodizing time and reaches maximum of 216 nm at 25 min, and it doesn't change between 25 and 35 min, then decreases with prolonging the period of anodizing. In other two solutions, the variation of membrane thickness is similar to that in 4% solution, except for the moment of reaching maximum of thickness and beginning to become thinning. The maximums of thickness are 146 nm and 105 nm respectively for 10% and 18.5% solution. The lower acid content is beneficial to gaining thicker membrane.

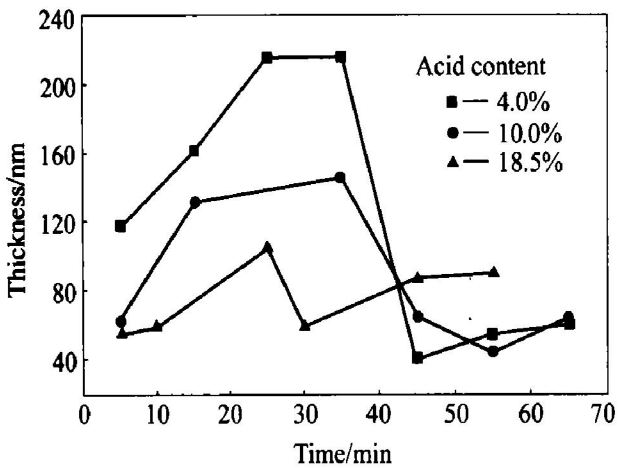

Fig. 1 Correlation of membrane thickness with content of electrolyte and anodizing time

During anodizing, there are two reactions occurring in the same time. On the one hand, aluminum is oxidized by electrochemistry reactions[26]:

$$Al - 3e^- \rightarrow Al^{3+} \quad (1)$$

$$2Al^{3+} + 3O^{2-} \rightarrow Al_2O_3 \quad (2)$$

These reactions bring about increment of membrane thickness. On the other hand, aluminum oxide can react with phosphoric acid:

$$Al_2O_3 + 2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2O \quad (3)$$

It can cause alumina layer on the Al foil to be solved, resulting in thinning of membrane.

At the original stage, e. g. before the first 10 min in Fig. 1, aluminum oxidization is dominant process. When the speed of Al is equal to that of alumina solving, the thickness keeps unchangeable, e. g. the thickness of alumina keeps unchangeable from 22 min to 37 min in 4% phosphoric acid solution. However, the anodization is a exothermal process, and it will cause temperature rising in the vicinity of Al anode. This can accelerate severely reaction (3)[26]. In addition, the resistance of Al anode will rise with thickness increment of alumina layer on foil. Thus, exothermal process can become acute much more. So, the speed of alumina solving increases greatly. This brings about the decrease in the thickness of membrane when the period of anodizaition has been prolonged. In addition, the higher the acid content, the more alumina solves quickly.

Fig. 2 shows the microstructures of AAO membrane. Nanopores distribute evenly in the membrane with an average pore diameter around 70 nm,

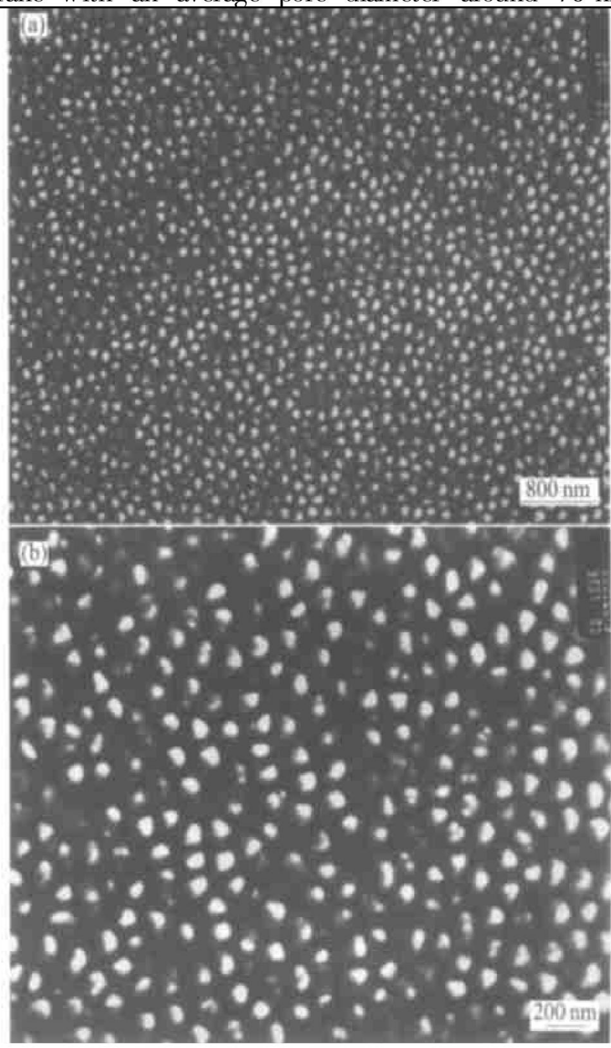

Fig. 2 TEM images of AAO membrane stripped from pure Al foil

average center-to-center distance between pores about 125 nm, and pore density exceeding $10^{10}/cm^2$.

Fig. 3 shows TEM images of membrane stripped from Al-Mg-Mn alloy foil anodized in the same condition with pure aluminum. The integration of membrane is damaged by adding alloying elements, Mg and Mn. They bring about the uneven distribution of the pores, even forming large black stain or distinct defect in the membrane. The black stain may correlate with solubility of magnesium oxide and manganese oxide in phosphoric acid solution. But the real cause needs to be investigated further. It can be seen that the purity of aluminum foil is an important parameter to the quality of membrane.

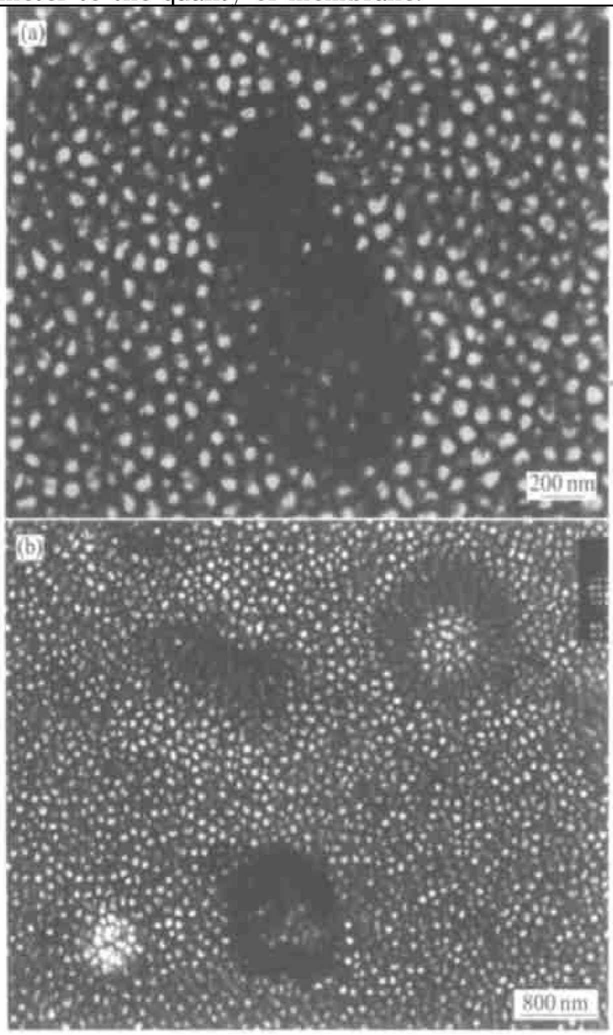

Fig. 3 TEM images of anodic membrane separated from Al-Mg-Mn alloy foil

In order to seek the method improving the crystal structure of membrane, some samples obtained by anodizing pure aluminum were annealed at 600 ℃ for 24 h and others at 930 ℃ for 3 h in air. Their X-ray diffraction patterns are showed in Fig. 4 and Fig. 5 respectively.

By comparing Fig. 4 with Fig. 5, it can be seen that the membrane is amorphous still after being annealed at 600 ℃ for 24 h. But, when the sample was

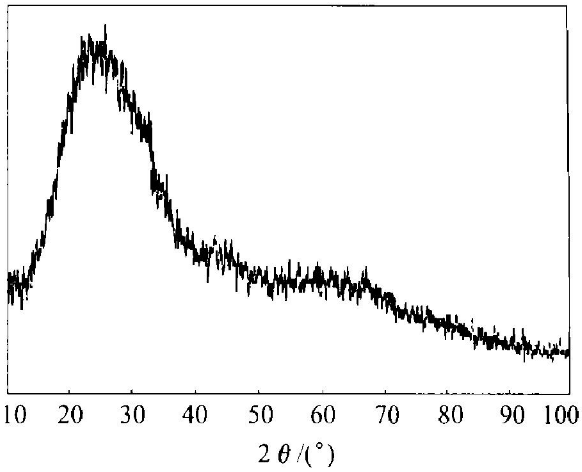

Fig. 4 X-ray diffraction pattern of AAO membrane annealed at 600 ℃ for 24 h in air

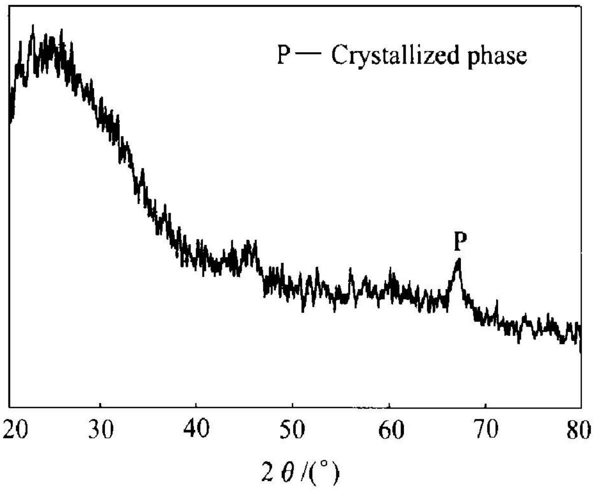

Fig. 5 X-ray diffraction pattern of AAO membrane annealed at 930 ℃ for 3 h in air

annealed at 930 ℃ for 3 h, there is an apparent peak (P) at diffractive angle of $2\theta = 67.122°$ in X-ray diffraction pattern. At the vicinity of this angle, there is an opportunity of occurring a diffractive peak of x-Al_2O_3, γ-Al_2O_3 or γ'-Al_2O_3. After comparing carefully diffractive peak with standard powder diffraction cards, it is found that the standard diffractive peak of γ-Al_2O_3 approach very much the result of this study (standard diffraction card number PDF# 10-0425). So, the diffraction peak in Fig. 5 belongs to γ-Al_2O_3. However, the peak is broad and weaker. It indicates that the annealing parameters are not the optimum.

4 CONCLUSIONS

1) When the pure Al foil is anodized in phosphoric acid solution, the thickness of anodic alumina decreases with increasing electrolyte content. For the certain phosphoric acid solution, there is an optimum time to gain the maximum of membrane thickness. In this study, the reached maximum of membrane thick-

ness is about 216 nm after having anodized pure aluminum for 25 min under a constant voltage of 40 V in 4% phosphoric acid solution.

2) The purity of aluminum is an important parameter for the quality of AAO membrane. The membrane with well-distributed nanometer pores can be obtained through anodizing high pure aluminum. The average pore diameter is about 70 nm, and the pore density exceeds $10^{10}/cm^2$. However, there are many defects in the membrane from anodizing Al-Mg-Mn alloy. Alloying elements can bring about large black stains or defects and damage the integration of membrane.

3) The obtained AAO membrane by anodizing is amorphous. After being annealed at 600 ℃ for 24 h, it is still amorphous. It begins to transform to γ-Al_2O_3 when membrane is annealed at 930 ℃.

ACKNOWLEDGMENTS

The authors thank Professor Cheng S Q and Professor Guo Z Y for TEM check of samples.

REFERENCES

[1] Brace A. Seventy years of sulphuric acid anodizing[J]. Trans IMF, 1997, 75(5): B101.
[2] Itoh N, Kato K, Tsuji T. Preparation of a tubular anodic aluminum oxide membrane[J]. J Membrane Sci, 1996, 117: 189.
[3] Dickey E C, Varghese O K, Ong K G. Room temperature ammonia and humidity sensing using highly ordered nanoporous alumina films[J]. Sensors, 2002, 2: 91.
[4] Mikulskas I, Juodkazis S, Jagminas A. Aluminum oxide film for 2D photonic structure: room temperature formation[J]. Optical Materials, 2001, 17: 343.
[5] Holland E R, Li Y, Abbott P. Large area gridded field emitter arrays using anodized aluminum[J]. Displays, 2000, 21: 99.
[6] Tatarenko N I, Mozalev A M. Geometry and element composition of a nanoscale field emission array formed by self-organization in porous anodic aluminum oxide[J]. Solid-State Electronics, 2001, 45: 1009.
[7] Huber C A, Huber T E, Sadoqi M. Nanowire array composites[J]. Science, 1994, 263: 800.
[8] Masuda H, Yasui K, Nishio K. Fabrication of ordered arrays of multiple nanodots using anodic porous alumina as an evaporation mask[J]. Advanced Materials, 2000, 12(14): 1031.
[9] Zeng H, Zheng M, Skomski R, et al. Magnetic properties of self-assembled Co nanowires of varying length and diameter[J]. J Appl Phys, 2000, 87(9): 4718.
[10] Peng Y, Qin D H, Zhou R J. Bismuth quantum-wires arrays fabricated by electrodeposition in nanoporous anodic aluminum oxide and its structural properties[J]. Mater Sci and Eng, 2000, B77: 246.
[11] Forrer P, Schlottig F, Siegenthaler H. Electrochemical preparation and surface properties of gold nanowire arrays formed by the template technique[J]. J Appl Electrochem, 2000, 30: 533.
[12] Pan S L, Zeng D D, Zhang H L. Preparation of ordered array of nanoscopic gold rods by template method and its optical properties[J]. Appl Phys A, 2000, 70: 637.
[13] Zhang X, Yao B, Zhao L. Electrochemical fabrication of single-crystalline anatase TiO_2 nanowire arrays[J]. J Electrochem Soc, 2001, 148(7): G398.
[14] Zhu H, Yang S, Ni G. Study on magnetic property of $Fe_{14}Ni_{86}$ alloy nanowire array[J]. J Magn Magn Mater, 2001, 234: 454.
[15] Xu D, Shi X, Guo G. Electrochemical preparation of CdSe nanowire arrays[J]. J Phys Chem B, 2002, 104: 5061.
[16] Zhang L D, Mou J M. Nanometer Materials and Nanostructure[M]. Beijing: Science Press, 2001. 51.
[17] Maier S A, Brongersma M L, Kik P G. Plasmonics– a route to nanoscale optical devices[J]. Advanced Materials, 2001, 13(19): 1501.
[18] Terris B D. Patterning magnetic films by ion beam irradiation[J]. J Appl Phys, 2000, 87(9): 7004
[19] Yamashita I. Fabrication of a two-dimensional array of nano-particles using ferritin molecule[J]. Thin Solid Films, 2001, 393: 12.
[20] Wang Z L, Harfenist S A, Whetten R L. Bundling and interdigitation of adsorbed thiolate groups in self-assembled nanocrystal superlattices[J]. J Phys Chem B, 1998, 102: 3068.
[21] Harfenist S A, Wang Z L, Whetten R L. Three-dimensional hexagonal close-packed superlattice of passivated Ag nanocrystals[J]. Advanced Materials, 1997, 9(10): 817.
[22] LI Mei, et al. Coupled synthesis and self-assembly of nanoparticles to give structures with controlled organization[J]. Nature, 1999, 402(25): 393.
[23] Murray C B, et al. Colloidal synthesis of nanocrystals and nanocrystal superlattices[J]. IBM J Res Dev, 2001, 45(1): 47.
[24] Herrero E, Buller L J, Abruna H D. Underpotential deposition at single crystal surfaces of Au, Pt, Ag and other materials[J]. Chem Rev, 2001, 101: 1897.
[25] Boontong Y. Templated aqueous syntheses of inorganics within carboxyl-containing block copolymer domains[D]. Massachusetts Institute of Technology, 2002.
[26] Diggle J W, Downie T C, Goulding C W. Anodic oxide flims on aluminum[J]. Chem Rev, 1969, 69: 365.

(Edited by YANG Bing)