

Structure of Oxide Film Prepared by Two-step Anodization of Aluminum

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The effect of pre-existing barrier-type film on porous aluminum oxide film formation during anodization was investigated to control the uniform film growth rate. Initial potential fluctuations during anodization indicated that the breakdown of barrier-film is preceded before the porous formation and the induction time for the porous film growth increases with the increases of pre-existing film thickness. The porous film growth mechanism is not affected by the presence of barrier film on aluminum surface. In parallel, uniform growth of barrier film underneath the porous structure was attained by two-step anodization processes.

Keywords : aluminum, anodization, oxide layer, potential transients.

1. Introduction

Metal aluminum is covered with protective oxide film in nature. Electrochemical oxidation of aluminum induces the structural change of both metal aluminum and surface oxide film. Exposure to aggressive anions such as chloride ions causes the local breakdown of oxide film and the following dissolution of metal aluminum.¹⁾⁻²⁾ However, when metal aluminum is anodized in low pH solution at low temperature or in neutral solution, anodic oxide film is formed on the metal surface and its structure becomes different according to the several anodizing parameters such as nature of solution, temperature, anodizing voltage.³⁾⁻⁵⁾ Porous-type oxide film is formed when it is slightly soluble. On the other hand, a compact and dense barrier-type film is formed when it is insoluble.

Porous-type film is a partly hydrated aluminum oxide, which consists of thin barrier layer and porous overlayer. After anodization, irregularly ordered pore arrangement was appeared on the top surface but the ordered region exists at the bottom of pores. Masuda et. al. developed a repetitive formation and dissolution of oxide layer to obtain the regularly spaced nano-pore structure.⁶⁾ Irregular porous alumina was totally removed and the remaining concave texture works as pore initiation sites in the following anodization steps.⁷⁾ Pore diameter, inter-pore distance, and film thickness depend on the applied anodizing voltage and electrolyte composition.⁸⁾ The pore

channel structure is straight and parallel, and a high aspect ratio over 1,000.

Highly-ordered nano-porous alumina has been actively applied as a template structure for the fabrication of nano-size materials, such as Cu₂O, ZnO and LiCoO₂.⁹⁾ Recently, the application of nano-porous alumina was expanded to the surface treatment of aluminum alloy, which is the structural materials of devices including etcher, asher, and susceptor, for the fabrication of liquid crystal display. These devices are exposed to the aggressive environments such as plasma etching and the durable and uniform thickness of porous film is very important factors for diverse applications. Since the heating element is inserted inside bulk aluminum base structure, the welding is required and the formation of interface between welding rod and Al structure materials results in the nonuniform thickness of porous oxide film on the surface during anodization. Porous film grows faster on welding part and non-uniformity of film thickness reaches up to 30%. Its nonuniformity can be overcome by the formation of barrier oxide film which can work as a resistor for further surface reaction.

In this work, thin barrier-layer oxide film was electrochemically grown on aluminum surface and the effect of barrier-layer on the subsequent porous film growth was investigated to induce the uniform growth of porous oxide film. In parallel, the possibility of barrier film growth present underneath the pore structure was investigated by two successive anodizing in different electrolytes.

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2. Experimental

A high purity aluminium foil (thickness: $110\ \mu\text{m}$, purity 99.99%, Toyo, Japan) was used in the experiment. In order to remove the air-formed oxide film, specimen were electropolished at 21 V below 0C for 4 min in a mixed solution of HClO_4 (Aldrich) and $\text{C}_2\text{H}_5\text{OH}$ (Aldrich).

For the formation of barrier-type oxide film on aluminum, aluminum was anodized in 0.07 M ammonium pentaborate octahydrate (Junsei, Japan) solution at $25\text{ }^\circ\text{C}$ by galvanostatic method. Porous-type oxide film was anodically obtained in 0.3 M sulfuric acid (Aldrich) solution by applying 25 V at $0\text{ }^\circ\text{C}$. The effect of barrier film on the growth rate of porous film was investigated with the two successive anodizations in different electrolyte and electrical synthetic conditions. Potential transients during oxide film formation were measured with digital multimeter (KEITHLEY 2000). Surface morphology was observed with scanning electron microscope (SEM, Hitach S-4300).

3. Results and discussion

Fig. 1 shows the surface of porous alumina film formed on aluminum during anodization in an acid electrolyte. Porous-type oxide film is consisted of thin barrier layer and porous overlayer. Pore formation begins by the local distribution of electric field on the nonconductive natural oxide film. It results in the field-enhanced dissolution of the oxide film and a subsequent stable pore growth.⁹⁾ Prior to anodization, metal aluminum was electropolished to remove an air-formed oxide film and smooth the surface. Its surface roughness measured by atomic force microscopy was estimated to be $0.734\ \text{nm}$ over $3\ \mu\text{m}^2$. Fig. 2(a) shows the cross section view of porous alumina structure of Fig. 1, which was grown to be $4.5\ \mu\text{m}$ during 3 hr of anodization. It is commensurate with the film growth rate of $1.5\ \mu\text{m/hr}$.

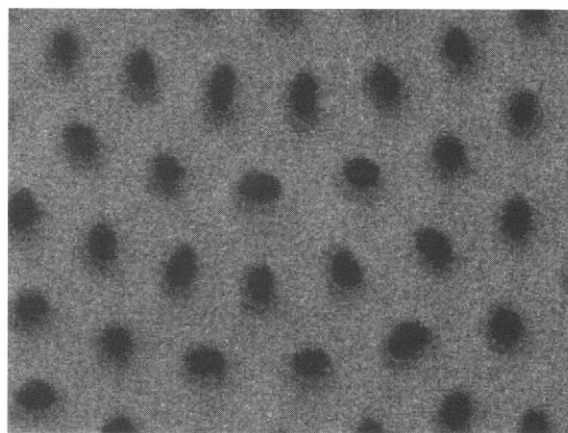


Fig. 1. Surface of porous alumina film prepared by anodization.

In order to investigate the effect of presence of barrier film on the growth of porous film during anodization, barrier-type film was pre-formed by anodization in ammonium borate solution. The thickness of barrier oxide film was controlled by adjusting the anodization voltage since the barrier-type film growth rate is $1.4\ \text{nm/V}$.¹⁰⁾ The presence of $10\ \text{nm}$ -thick film decreases the porous film thickness to be $3.5\ \mu\text{m}$, as shown in Fig. 2(b). When the film thickness was increased to be $20\ \text{nm}$, Fig. 2(c) shows the formation of only $3\ \mu\text{m}$ -thick oxide film. However, pore channel has the straight and parallel structure which was not affected by the presence of barrier oxide film. Fig. 3 indicates that porous film growth rate was decreased at a rate of $0.025(\mu\text{m/hr})/(\text{nm of barrier film thickness})$. Fig. 4 shows the potential transients during porous film formation. It was measured between working electrode and counter electrode. In case of specimen without the barrier-oxide film, Fig. 4(a) shows that a sudden potential rise appears initially by the formation of barrier-type film and potential increases slowly by the growth of porous film. However, Fig. 4(b) of sample with $10\ \text{nm}$ -thick barrier film shows the large fluctuation of potential during incipient 200 s of anodization. Polarity change during

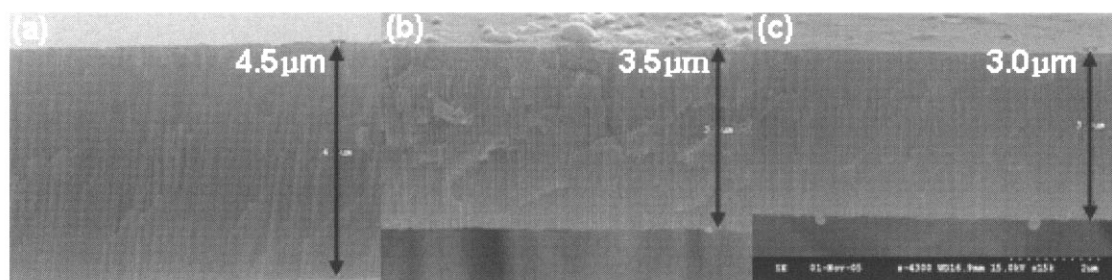


Fig. 2. Cross section view of porous alumina structure. Barrier-type film was intentionally grown on aluminum surface before the anodization in a sulfuric acid. (a) without a barrier film, thickness of barrier film; (b) 10 nm, (c) 20 nm.

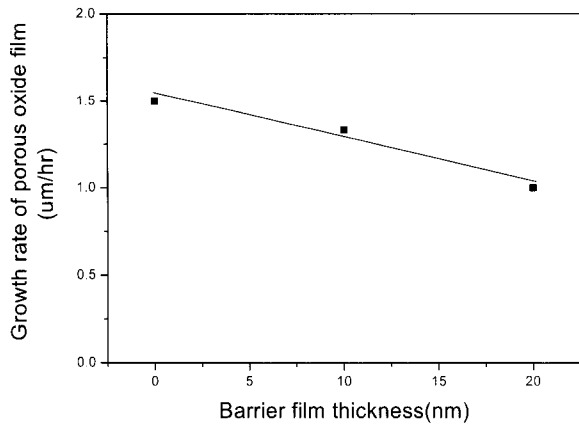


Fig. 3. The effect of the presence of barrier-type film on porous film grow rate. (a) without a barrier film, thickness of barrier film; (b) 10 nm, (c) 20 nm.

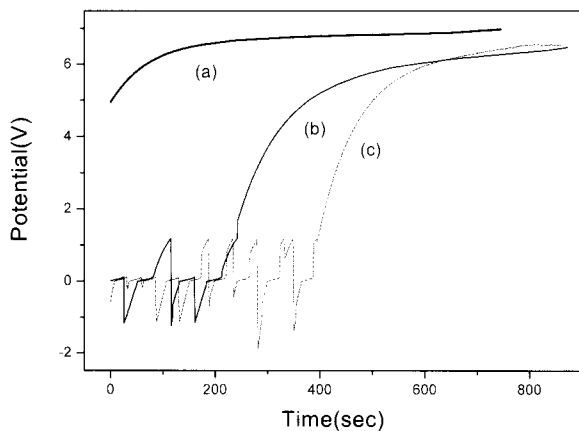


Fig. 4. Potential transients during the anodization in a sulfuric acid. (a) without a barrier film, thickness of barrier film; (b) 10 nm, (c) 20 nm.

potential fluctuation suggests that dominant reaction on the aluminum surface can be cathodic reaction at the negative potential value. The only possible cathodic reaction is considered to be the reduction of proton in acid solution. Alwitt et. al. reported the current efficiency of 110-115% during electrochemical dissolution of aluminum,¹¹⁾ which manifests the hydrogen evolution reaction on the actively dissolving aluminum surface. It suggests that bare aluminum surface was exposed to anodizing solution during the initial potential fluctuation by the breakdown of barrier-type oxide film. Rapid potential increase following potential fluctuation can be ascribed to the formation of anodic compact film growth. Porous film growth over compact film was followed during slow potential increase. Potential fluctuation becomes more evident when 20 nm-thick barrier film covers the aluminum surface. As the barrier film becomes thick, the time to breakdown the barrier film increases. Once the film

breakdown occurs, the porous film growth mechanism is the same as the specimen without barrier film.

Under severe aggressive environments such as plasma etching, a robust and durable oxide film structure is required since porous alumina can be destroyed with time. Porous film has a nanometer-thick barrier film underneath the porous structure. Since the barrier film is compact and dense, the increase of barrier film thickness can enhance the durability and reliability of aluminum oxide film. Firstly, aluminum is anodized in a sulfuric acid solution and secondly, reanodized in ammonium borate solution. Fig. 5 shows the structure of oxide film which shows the increase of barrier film thickness beneath the pore structure. During second anodization, it is expected that

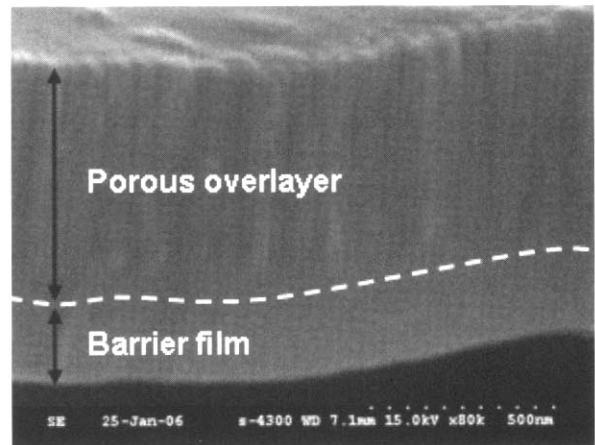


Fig. 5. Cross section view of oxide film which shows the increase of barrier film thickness beneath the pore structure. [first anodization in a sulfuric acid and second anodization in ammonium borate solution.]

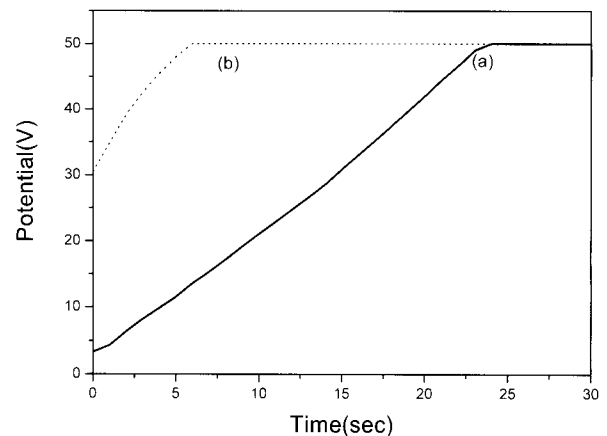


Fig. 6. Potential increase rate during barrier film formation on (a) the electropolished flat surface and (b) the bottom of 3 μm pore structure. [applied current density: 30 mA/cm², electrolyte: 0.3 M sulfuric acid]

electric field is only existing at the bottom of pore structure and the growth of barrier film should be confined to this place since the electrolyte can only penetrate into the pore bottom. Contrary to the expectation, the uniform thickness of barrier film is obtained. However, the pore channel width decreases and becomes tortuous, which suggests the nonuniform thickening of pore walls. Fig. 6 shows the comparison of potential increase rate during barrier film formation on the electropolished flat surface and the bottom of 3 μm -long pore structure. Electropolished surface is considered to be clean surface without oxide layer on it. When 30 mA/cm² is applied, 70 nm-thick barrier film is formed during 25 sec and it is equivalent to 2.8 nm/s of growth rate. When the same anodization process is performed for the specimen with 3 μm -long pore structure, potential suddenly jumps to 30 V due to pre-existing porous film and increases up to 50 V during 7 sec. This potential rise indicates the 4 nm/s of barrier film growth rate under pore structure. This growth rate is 40% faster than that of electropolished surface, but the reason for rapid growth rate is unclear yet. However, the rapid conversion of outer hydrated oxide film of porous film into barrier layer might be responsible for the rapid potential increase, i.e., a faster film growth rate.

4. Conclusions

Firstly, barrier-type oxide film was intentionally grown on aluminum surface in a neutral solution and porous oxide film was fabricated by anodization in a sulfuric acid solution. As the thickness of barrier film increases, the porous film growth rate decreases at a rate of 0.025($\mu\text{m}/\text{hr}$)/(nm of barrier film thickness). Initially measured potential transients support the breakdown of barrier-film by the detection of cathodic hydrogen evolution reaction

before the porous film formation. Simultaneously, the induction time for the porous film formation also increases with the increases of pre-existing barrier film thickness but the porous film growth mechanism is not affected by the presence of barrier-film before anodization. In order to obtain a robust and durable oxide film structure, increase of barrier film thickness underneath the porous structure was attained by two-step anodization processes.

Acknowledgement

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References

1. C. G. Dunn, R. B. Bolon, A. S. Alwan, and A. W. Stirling, *J. Electrochem. Soc.*, **118**, 381 (1971).
2. H. H. Strehblow, *Werkstoffe and Korrosion*, **35**, 473 (1984).
3. J. W. Diggle, T. C. Downie, and C. W. Goulding, *Chem. Rev.*, **69**, 365 (1968).
4. J. Choi, Y. Luo, R. B. Wehrspohn, R. Hillerbrand, and U. Gosele, *J. Appl. Phys.*, **94**, 4757 (2003).
5. V. P. Parkhutik and V. I. Shershulsky, *J. of Physics D- Applied Physics*, **25**, 1258 (1992).
6. H. Masuda and K. Fukuda, *Science*, **268**, 1466 (1995).
7. H. Masuda and M. Satoh, *Jpn. J. Appl. Phys.*, **35**, L126 (1996).
8. G. E. Thomson, R. C. Furneaux, G. C. Wood, J. A. Richardson, and J. S. Goode, *Nature*, **272**, 433 (1978).
9. J. Oh, Y. Jung, J. Lee, and Y. Tak, *Studies in Surface Science and Catalysis*, **146**, 205 (2003).
10. K. R. Hebert and R. C. Alkire, *J. Electrochem. Soc.*, **135**, 2247 (1988).
11. R. S. Alwitt, H. Uchi, T. R. Beck, and R. C. Alkire, *J. Electrochem. Soc.*, **131**, 13 (1984).