Anodizing of Aluminum Coated with Zirconium Oxide by a Sol-Gel Process I. Effect of Heat Treatment on the Formation of the Anodic Oxide Film

Keiji WATANABE,* Masatoshi SAKAIRI, Hideaki TAKAHASHI, Katsumi TAKAHIRO^a,
Shinji NAGATA^a and Shinji HIRAI^b

Graduate School of Engineering, Hokkaido University, (N13, W8, Kita-Ku, Sapporo 060-8628, Japan)

^aInstitute for Materials Research, Tohoku University, (Katahira-2, Aoba-Ku, Sendai 980-8577, Japan)

^bDepartment of Materials Science and Engineering, Muroran Institute of Technology, (Mizumoto-cho, Muroran-shi, Hokkaido 050-8585, Japan)

Received June 15, 1999 ; Accepted August 26, 1999

Aluminum specimens were covered with zirconium oxide films by sol-gel dip coating at $T_h=573$ and 873 K, and then anodized galvanostatically in a neutral borate solution. The time-variation in the anode potential during anodizing was monitored, and the structure of anodic oxide films was examined by TEM, EDX, and RBS. During anodizing of specimens coated with ZrO_2 at $T_h=573$ K, the anode potential, E_a , increased linearly with time, t_a , and the slope of the E_a vs. t_a curve increased with increasing the number of sol-gel coatings. An anodic oxide film, which was composed of an inner Al_2O_3 layer and an outer Al-Zr composite oxide layer, grew at the interface between the ZrO_2 layer and metal substrate during anodizing. The thickness of the inner layer increased with t_a , whereas the thickness of the outer layer showed a maximum before decreasing with t_a . Specimens coated with ZrO_2 at $T_h=873$ K showed E_a jumps between 40 and 110 V just after the commencement of anodizing, and then a slow E_a increase. An anodic oxide film composed of a single layer of Al_2O_3 , formed beneath the ZrO_2 layer during anodizing. The mechanism of the formation of anodic oxide films on aluminum coated with ZrO_2 films is discussed in terms of ion transport across the anodic oxide film.

Key Words : Sol-gel Coating, Anodizing of Aluminum, Zirconium Oxide, Composite Oxide Film

1 Introduction

Anodic oxide film formed on aluminum has an important role as dielectric films in aluminum electrolytic capacitors. Recent development of electronics requires smaller electrolytic capacitors with higher electric capacitance. The electric capacitance, C , of the electrolytic capacitor is expressed by the following equation.

$$C = \epsilon_0 \epsilon S / \delta \quad (1)$$

where, ϵ_0 is the vacuum permittivity, ϵ the specific dielectric constant of the anodic oxide film, S the surface area, and δ the film thickness. Eq. (1) indicates that C is proportional to ϵ and S , and inversely proportional to δ . Increases in S , hence lead to increases in C , and can be achieved by electrolytic etching of the aluminum substrate before anodizing.¹⁾ Decreases in δ can be achieved by forming anodic oxide films containing crystalline oxides, since these can sustain higher electric fields than amorphous anodic oxide films. Anodizing after hydrothermal or thermal treatments causes the formation of anodic oxide films containing γ - Al_2O_3 , leading to a 0.8-1.0 nm/V K -value, which is the ratio of the film thickness to the film formation potential.²⁻⁵⁾

Increases in ϵ are possible by forming composite

oxide films on aluminum, in which valve metal oxides like TiO_2 , ZrO_2 , and etc. are incorporated. In previous investigations with reference to the formation of Al-Ti composite oxide films by using a pore-filling method⁶⁾ and MOCVD/anodizing,⁷⁾ it was found that the parallel capacitance of the Al-Ti composite oxide film is 60 % higher than that of barrier type anodic oxide films on aluminum.

In the present investigation, the combination of sol-gel coating with anodizing was used to form Al-Zr composite oxide films. Aluminum specimens were coated with ZrO_2 gel film by dipping into sol solution, and then heated at 573 K and 873 K. The specimens coated with ZrO_2 were anodized in a neutral borate solution to obtain the Al-Zr composite oxide films. The structure and dielectric properties of the anodic oxide films were examined as functions of the heating temperature and the number of dipping/heating cycles in the ZrO_2 coating. The results are reported in two successive papers. In the present paper, the structure and formation mechanism of the anodic oxide films are discussed, and it will be followed by a further paper describing the relationship between the film structure and its dielectric properties.

2 Experimental Procedure

2.1 Specimen

Aluminum foil (purity: 99.99 %) was used as specimens ($2 \times 2 \text{ cm}^2$ with handle) after electropolishing in a perchloric acid/acetic acid mixture.

2.2 Sol-gel coating

Electropolished specimens were coated with ZrO_2 films by sol-gel dip-coating with the procedure indicated in Fig. 1.^{8,9)} The specimens were dipped into a mixture of zirconium tetra-normal butoxide, diethylene-glycol, distilled water, and dehydrated ethanol. After withdrawn from the solution with the velocity of 3 mm/s, the specimens were dried at room temperature in air. The dried specimens were heated at 573 K in pure oxygen for 30 min to obtain the ZrO_2 films. The operations described above were repeated n times ($n=2\sim6$), in order to change the thickness of ZrO_2 films. At the final step, the specimens with ZrO_2 films were heated in pure oxygen for 30 min at $T_h=573$ or 873 K.

2.3 Anodizing

The specimens coated with ZrO_2 film were anodized in 0.5 M ($\text{M}=\text{mol dm}^{-3}$)- H_3BO_3 /0.05 M- $\text{Na}_2\text{B}_4\text{O}_7$ solution (pH=7.4) at $T_a=293 \text{ K}$ with a constant current of $i_a=10 \text{ A/m}^2$, and the change in the anode potential (vs. Ag/AgCl KCl sat.) with time (E_a vs. t_a curve) was monitored by a digital multi-meter connected with a PC system. Electropolished specimens without ZrO_2 film were also anodized under the same conditions, to establish the effect of the ZrO_2 films on anodic oxide film formation.

2.4 Characterization of films

2.4.1 Transmission electron microscopy (TEM)

Encapsulated specimens were first trimmed, and then sliced into 40 nm thick sections, using an ultrami-

Fig. 1 Diagram of procedures of the sol-gel coating to form ZrO_2 films.

crotope (REICHERT-NISSEI ULTRA CUTS E) with a diamond knife (Diatome Ltd. DIATOME ULTRA). Slices of the vertical section of the specimens were then examined under a HITACHI H-700H TEM at 200 kV, and analyzed with an energy dispersive X-ray analyzer (EDX) equipped with another TEM (JEOL JEM-2000ES).

2.4.2 Rutherford backscattering spectroscopy (RBS)

Anodic oxide films were analyzed by RBS (HIGH VOLTAGE ENGINEERING 1.7MV TANDETRON), using 2.0 MeV of a He^{2+} ion beam supplied by a Van de Graff accelerator. The He^{2+} ion beam angle was normal to the specimen surface, and the detector angle was 170° to the incident direction. The chemical composition of the anodic oxide films were determined, using the RUMP program.¹⁰⁾

3 Results

3.1 Formation of ZrO_2 layer by sol-gel coating

Figure 2 shows TEM images of the cross section of specimens covered with ZrO_2 film. Here, the dipping/heating cycle was repeated 4 times ($n=4$), and heating at the final step was conducted at a) $T_h=573 \text{ K}$ or b) $T_h=873 \text{ K}$. Zirconium oxide layers coated at both T_h have uniform thicknesses of about 220 nm. Electron diffraction (ED) analysis suggests that ZrO_2 coated at $T_h=573 \text{ K}$ is amorphous, whereas at $T_h=873 \text{ K}$ it has a fluorite-type crystal structure, consistent with the results by Takahashi *et al.*¹¹⁾ There appear cracks perpendicular to the metal substrate in the ZrO_2 layer at $T_h=873 \text{ K}$ due to mechanical damage by the diamond knife, and this suggests poorer ductility than the ZrO_2 layer at $T_h=573 \text{ K}$.

3.2 Formation of anodic oxide films after ZrO_2 coating

Figure 3 shows E_a vs. t_a curves for specimens coated with ZrO_2 layers at $n=2\sim6$ and a) $T_h=573 \text{ K}$ or b) $T_h=873 \text{ K}$. In Fig. 3, the E_a vs. t_a curve for electropolished specimens without ZrO_2 is also indicated as a

Fig. 2 Transmission electron micrographs of vertical cross sections of specimens coated with ZrO_2 by sol-gel coating with $n=4$ at T_h =a) 573 K or b) 873 K. Electron diffraction patterns of the ZrO_2 coated layers are shown as insets. Conditions of coating as in Fig. 1.

solid curve. The specimen without ZrO_2 shows a linear increase in E_a with t_a . Specimens coated with ZrO_2 at $T_h=573$ K (see Fig. 3-a) show a 10-15 V jump in E_a just after the commencement of anodizing, and the E_a -jump does not depend on n . After the initial stage, E_a increases linearly with t_a . The slope of E_a vs. t_a curves for ZrO_2 -coated specimens is much steeper than that without a ZrO_2 layer, and it increases with the number of dipping/heating cycles, n .

Specimens coated at $T_h=873$ K (see Fig. 3-b) show a 40-110 V-jump in E_a just after the commencement of anodizing, and the E_a -jump increases with n . After an initial transient period, E_a increases slowly with t_a , and then the rate of increase in E_a reaches a steady value, similar to that of the specimens without ZrO_2 . The slow increase in E_a at the early stage was accompanied by gas evolution.

3.3 Structure of anodic oxide films formed after ZrO_2 coating at $T_h=573$ K

Figure 4 shows TEM images of cross sections of specimens anodized up to a) $E_a=200$ V and b) $E_a=400$ V after ZrO_2 coating with $n=4$ at $T_h=573$ K. The anodized specimens show two layers between the ZrO_2 layer and the metal substrate: an outer dark layer and an inner light-gray layer. The outer layer is much thicker at $E_a=200$ V than at $E_a=400$ V, whereas the inner layer is much thinner at $E_a=200$ V than at $E_a=400$ V.

Figure 5 shows a) the RBS spectrum obtained for specimens anodized up to $E_a=400$ V after ZrO_2 coating with $n=4$ at $T_h=573$ K, and b) the concentration depth-profile of Zr, Al, and O, derived from the RBS

spectrum using the RUMP program.¹⁰⁾ Figure 5-b suggests that the outer dark layer in Fig. 4 consists of an Al-Zr composite oxide layer, and that the inner light-gray layer consists of an alumina layer. Hafnium included in the ZrO_2 layer comes from impurities in the Zr-alkoxide. The EDX analysis of the Al-Zr composite oxide layer estimated the Al concentration to be about 15 %.

Figure 6 shows the change in the thicknesses of the outer Al-Zr composite oxide layer, δ_c (Fig. 6-a), and of the inner alumina layer, δ_a (Fig. 6-b), with anodizing time, t_a , after ZrO_2 coating with different n at

Fig. 4 Transmission electron micrographs of cross sections of specimens anodized up to E_a =(a) 200 V and (b) 400 V after ZrO_2 coating with $n=4$ at $T_h=573$ K. Conditions of coating as in Fig. 1, and anodizing as in Fig. 3.

Fig. 3 Change in anode potential, E_a with time, t_a , during anodizing in 0.5 M- H_3BO_3 /0.05 M- $\text{Na}_2\text{B}_4\text{O}_7$ solution at 293 K and 10 A/m², obtained for specimens coated with ZrO_2 at T_h =a) 573 K or b) 873 K.

Fig. 5 a) RBS spectrum and b) concentration profiles of Zr, Al, O, and Hf in depth for specimens anodized up to $E_a=400$ V after ZrO_2 coating with $n=4$ and $T_h=573$ K. Conditions of anodizing as in Fig. 3.

Fig. 6 Changes in the thickness of the outer layer, δ_c , and the inner layer, δ_a , with t_a , for specimens after ZrO_2 coating at $T_h=573$ K. Conditions of anodizing as in Fig. 3.

$T_h=573$ K. The change in the thickness of anodic oxide films formed on aluminum without ZrO_2 with t_a is shown as a solid curve in Fig. 6. The film thickness of the specimen without ZrO_2 shows a linear increase with t_a , but the change in δ_a with t_a is complicated and different for different n values. At the initial stage, all the δ_a vs. t_a curves of ZrO_2 -coated specimens show a slope similar to that of the specimen without ZrO_2 . In the later stage, the slope becomes flatter for specimens with $n=2$, while the slope becomes steeper for specimens with $n=4$ and 6. The tendency towards upward deviation in the slope becomes more remarkable with increasing n .

The thickness of the outer Al-Zr composite oxide layer, δ_c , on all the specimens coated with ZrO_2 at $T_h=573$ K shows an increase in the initial stage and then decreases after a maximum. The maximum δ_c value increases with increasing n .

3.4 Structure of anodic oxide films formed after ZrO_2 coating at $T_h=873$ K

Figure 7 shows TEM images of cross sections of specimens anodized up to a) $E_a=200$ V and b) $E_a=400$ V after ZrO_2 coating with $n=4$ at $T_h=873$ K. It can be seen from Fig. 7 that an oxide layer grows at the interface between the ZrO_2 layer and the metal substrate during anodizing, and that crystalline oxide is formed at the middle part of the oxide layer. The EDX and ED analyses suggested that the oxide layer is composed of Al_2O_3 , and that the crystalline oxide is $\gamma\text{-Al}_2\text{O}_3$. Figure 8 shows the change in the thickness of the alumina layer, δ_a , with anodizing time, t_a , after ZrO_2 coating with different n at $T_h=873$ K. The δ_a increases slowly with time, t_a , in the initial stage of anodizing, and then increases at a high rate in the later stage. The rate of increase in δ_a at the initial period increases with increasing n , whereas the rate

Fig. 7 Transmission electron micrographs of vertical sections of specimens anodized up to E_a =a) 200 V and b) 400 V after ZrO_2 coating at $n=4$ and $T_h=873$ K. Conditions of coating as in Fig. 1, and anodizing as in Fig. 3.

Fig. 8 Changes in the thickness of the Al_2O_3 layer with anodizing time, t_a , obtained for specimens after ZrO_2 coating with $T_h=873$ K. Conditions of anodizing as in Fig. 3.

of increase in δ_a at the later stage does not depend on n .

4 Discussion

4.1 Growth mechanism of anodic oxide films after ZrO_2 coating at $T_h=573$ K

Figure 9-a shows a schematic model of the formation of the anodic oxide film during anodizing after ZrO_2 coating at $T_h=573$ K. The zirconium oxide layer is considered to have a network structure of micropores and cracks, which are formed by the evaporation of organic compounds during heating of the sol precursor film. The micro-pore network structure may be reduced in the inner parts of the ZrO_2 layer by the repetition of the dipping/heating, since the repetition would allow the sol solution to penetrate into micro cracks. During heat treatment, a thin thermal aluminum oxide film may also be formed at the interface between the ZrO_2 layer and metal substrate.⁴⁾

When the specimen coated by ZrO_2 at $T_h=573$ K is immersed in anodizing solution, water and electrolyte could penetrate into the micro-pore network in ZrO_2 ,

Fig. 9 Schematic illustrations of the formation of anodic oxide films after ZrO_2 coating at a) $T_h=573$ K and at b) $T_h=873$ K.

so that the ZrO_2 layer is not able to sustain an electric field. The small jump in E_a just after the commencement of anodizing (See Fig. 3-a) may be due to the aluminum thermal oxide layer rather than ZrO_2 layers. This may be understood by the fact that the jump in E_a does not depend on n . A similar jump in E_a has been observed in anodizing aluminum after heat treatment in air.⁴⁾

During anodizing after ZrO_2 coating, O^{2-} ions dissociated from water at the bottom of the ZrO_2 layer transport inwards across the anodic oxide film to form pure aluminum oxide at the interface between the inner Al_2O_3 layer and metal substrate. The outward transport of Al^{3+} ions may allow the formation of a composite oxide layer by filling the micro pores with Al_2O_3 at the interface between the outer composite oxide layer and the ZrO_2 layer. In addition to the formation of oxide at the two interfaces, a conversion of the composite oxide to Al_2O_3 may occur at the interface between the outer and inner layers, due to the outward transport of Zr^{4+} or ZrO^{2+} ions under the electric field across the composite oxide layer.

Assuming that the transport number of Al^{3+} and O^{2-} ions remains constant during anodizing, the growth mechanism of the outer and inner layers can be explained as follows. The downward deviation in the δ_a vs. t_a curve for the specimen with $n=2$ from that for the specimen without ZrO_2 coating may be concerned with the micro-pore network, and with the conversion rate of composite oxide to Al_2O_3 . The $n=2$ specimen may be considered to have the most developed micro-pore network structure especially at regions near the surface, and to have the slowest conversion, and this causes the downward deviation. With $n \geq 4$, the micro-pore network structure is reduced and the conversion

becomes faster as n increases, causing more upward deviation in the δ_a vs. t_a curve with the larger n .

The net rate of increase in δ_c is obtained by subtracting the conversion rate of the composite oxide layer at the interface between the inner and outer layers from the formation rate of the composite oxide layer at the interface between the outer and ZrO_2 layers. The fact that δ_c shows a maximum at the intermediate period of anodizing may be explained by a decrease in the formation rate of the composite oxide layer with t_a , due to a larger porosity at the outer region of the ZrO_2 layer.

4.2 Growth mechanism of anodic oxide films after ZrO_2 coating at $T_h=873$ K

The structure of the ZrO_2 layers formed at $T_h=873$ K is very different from that formed at $T_h=573$ K, showing fluorite-type crystals and no network of micro cracks. This causes the anodic oxide film to grow in a different way after the ZrO_2 coating.

Figure 9-b shows a schematic model of the anodic oxide film growth after ZrO_2 coating at $T_h=873$ K. Here, a dense crystalline ZrO_2 layer blocks the solution penetration, and it can sustain an anode potential, E_a . This may explain a relatively large jump in E_a , 40-110 V, at the very initial stage of anodizing (Fig. 2-b), and n dependence of the E_a -jump. The slow increase in E_a after the jump is due to O_2 evolution, and this is attributed to the electron conductivity of the ZrO_2 . In addition to O_2 evolution, O^{2-} ions are formed by water dissociation and transport inwards across the ZrO_2 layer to form an Al_2O_3 layer at the interface between the metal substrate and ZrO_2 . After the Al_2O_3 layer grows to a certain thickness, O_2 evolution slows down and the formation of Al_2O_3 becomes predominant.

The O^{2-} ions reaching the interface between the ZrO_2 and Al_2O_3 layers could either react with Al^{3+} ions to form Al_2O_3 there, or could transport further inwards across the Al_2O_3 layer to form Al_2O_3 at the interface between the Al_2O_3 layer and metal substrate. The formation of crystalline oxide layers at the middle part of the Al_2O_3 layer may be due to the crystallization of amorphous oxide under a high electric field, and thermal Al_2O_3 formed at ZrO_2 may act as crystal seeds in the crystallization of amorphous oxide.⁵⁾

5 Conclusion

The formation of Al-Zr composite oxide films on aluminum was attempted by sol-gel coating and subsequent anodizing, and the following conclusions may be drawn.

1. The zirconium oxide layer coated on aluminum substrates by sol-gel coating consists of an amorphous oxide at a heating temperature, $T_h=573$ K, and it is fluorite-type crystalline oxide at $T_h=873$ K.

2. Galvanostatic anodizing of aluminum coated with ZrO_2 at $T_h=573$ K leads to the formation of oxide films consisting of an outer Al-Zr composite oxide layer and an inner Al_2O_3 layer at the interface

between the ZrO_2 layer and metal substrate. The thickness of the inner layer, δ_a , increases with time, and the rate of increase in δ_a increases with increasing number of dipping/heating cycles, n . The thickness of the outer layer, δ_c , initially increases with time, and then decreases after a maximum. This tendency is more pronounced for specimens with larger n -values.

3. Galvanostatic anodizing of aluminum coated with ZrO_2 at $T_h=873$ K leads to the formation of an Al_2O_3 layer at the interface between the ZrO_2 and metal substrate. The Al_2O_3 layer includes an $\gamma\text{-Al}_2\text{O}_3$ layer at the middle part.

Acknowledgments

The authors wish to thank K. Nishinaka, K. Dohjun, and R. Hasegawa of Muroran Institute of Technology for experimental assistance on the sol-gel coating. The work was financially supported by the Light Metal Education Foundation of Japan, and the Ministry of Education, Science, Sports and Culture, Japan with a Grand-in-Aid for Scientific Research on Priority Areas for "Electrochemistry of Ordered Interfaces"(No. 10131204). A part of this work was carried out under the Visiting Researcher's Program of the Institute for Materials Research, Tohoku University.

References

- 1) For example, R. S. Alwitt, H. Uchi, T. R. Beck, and R. C. Alkire, *J. Electrochem. Soc.*, **144**, 13 (1997).
- 2) H. Takahashi, Y. Umehara, T. Miyamoto, N. Fujimoto, and M. Nagayama, *J. Surf Finish. Soc. Jpn.*, **38**, 67 (1987).
- 3) H. Takahashi, Y. Umehara, R. Furuichi, and M. Nagayama, *J. Surf Finish. Soc. Jpn.*, **40**, 590 (1989).
- 4) H. Takahashi, C. Ikegami, M. Seo, and R. Furuichi, *J. Electron. Microsc.*, **40**, 101 (1991).
- 5) H. Takahashi, M. Dairaku, and M. Seo, *J. Surf Finish. Soc. Jpn.*, **45**, 810 (1994).
- 6) M. Shikanai, M. Sakairi, H. Takahashi, M. Seo, K. Takahiro, S. Nagata, and S. Yamaguchi, *J. Electrochem. Soc.*, **144**, 2756 (1997).
- 7) H. Takahashi, H. Kamada, M. Sakairi, K. Takahiro, S. Nagata, and S. Yamaguchi, *Meeting Abstracts of the 193rd meeting of the Electrochemical Society, Inc.*, No. 207 (1998).
- 8) S. Hirai, S. Aizawa, K. Shimakage, and K. Wada, *J. Japan Inst. Metals.*, **59**, 547 (1995).
- 9) S. Hirai, K. Shimakage, S. Aizawa, and K. Wada, *J. Am. Ceram. Soc.*, **81**, 3087 (1998).
- 10) L. R. Doolittle, *Nucl. Inst. Meth.*, **B15**, 227 (1986).
- 11) Y. Takahashi, K. Niwa, K. Kobayashi, and M. Matsuki, *Yogyo-Kyokai-Shi.*, **95**, 942 (1987).