A vacuum infiltration method was proposed to coat uniform zirconia (ZrO$_2$) films on etched aluminum (Al) foil. The formation behavior of the composite oxide films on aluminum (Al) foils with etch pits was different from that of flat Al foils. The multi-layer structures were formed on the ZrO$_2$-coated Al foil after being anodized. The formation mechanism of the multi-layer films on etched Al foils was discussed. The structure and composition of each layer were investigated by scanning electron microscopy and transmission electron microscopy. The multi-layer films consisted of an inner aluminum hydrate layer, middle Al$_2$O$_3$-ZrO$_2$ (Al-Zr) composite layer, and outer Al$_2$O$_3$ layer. Many Al$^{3+}$ ions passed through the coating layer and transferred into the inner layer. A particle-like and layered structure was observed in the inner layer. The formation of multi-layer films was mainly affected by the volume expansion of the outer Al$_2$O$_3$ layer and the dense middle Al-Zr composite oxide film. The ZrO$_2$ coated foils exhibited 26% higher specific capacitance than foils with only Al$_2$O$_3$ layer when being anodized at 600 V.

Experimental

Preparation processes of Al foils with multi-layer film. The coated foils were dried at 100 °C and annealed at 500 °C. The coating processes were repeated 4 times, and the coated samples were anodized at 600 V with 50 mA/cm$^2$ constant currents.

Figure 1. Preparation processes of Al foils with multi-layer film. The coated foils were dried at 100 °C and annealed at 500 °C. The coating processes were repeated 4 times, and the coated samples were anodized at 600 V with 50 mA/cm$^2$ constant currents.
Samples were anodized at 600 V with 50 mA/cm² constant currents in a boric acid (H₃BO₃) solution (100 g H₃BO₃/1 L H₂O) at 85°C for 50 min and then heated at 500°C for 2 min. In second step, the samples were anodized at 600 V for 5 min and heated at 500°C for 2 min. The samples without ZrO₂ were also anodized under the same conditions for comparison.

**Characterization.** — The cross-sectional morphologies of the samples were examined using field-emission scanning electron microscopy (FESEM, JEOL, JSM-6700F, Japan). The samples to be examined by TEM were thinned using a focused ion beam (FIB, FEI, versa 3D Lovac, USA). The structure and composition of the thin cross-section tunnels were characterized using field-emission transmission electron microscopy and energy dispersive X-ray spectroscopy (FETEM-EDS, FEI, Titan G2 ChemiSTEM Cs Probe, USA).

**Results and Discussion**

**Microstructure of oxide film layers.** — The cross-sectional structure of the coated and anodized tunnels was characterized by SEM and TEM. To obtain SEM images of the etch pits, the samples were polished and corroded in potassium hydroxide (KOH) solution for 2 min. Figure 3 shows the cross-sectional structures of coated and/or anodized tunnels. Figure 3a is an SEM image of the tunnel after coating, (b) is an SEM image of the tunnel after anodizing without coating, (c) is an SEM image of the tunnel after coating and anodizing, and (d) is a TEM image of the tunnel after coating and anodizing. As observed in Fig. 3a, a uniform ZrO₂ layer with 110-nm thickness was successfully coated on the etched Al foil. Empty space is observed between the ZrO₂ coating layer and the Al etch pit, which is caused by shrinkage during annealing at 500°C and corrosion by the KOH solution. The thickness of the anodized Al₂O₃ layer in Fig. 3b was approximately 610 nm. The ratio of the oxide thickness to the oxide formation voltage, K, is approximately 1.0 nm · V⁻¹, which is well matched with the reported K values of anodic oxide films of 0.8–1.3 nm · V⁻¹. The images in Figs. 3c and 3d reveal that a double layer structure was formed after coating and anodizing. In particular, the TEM image in Fig. 3d shows that the inner layer is composed of a particle-like and layered structure. The TEM image reveals that the inner layer is ZrO₂ and the outer layer is Al₂O₃. The thicknesses of the outer Al₂O₃ layers in the SEM and TEM images were approximately 520 nm and 530 nm, respectively. The K value of the Al₂O₃ layer in the Al foils with the ZrO₂ layer was approximately 0.87 nm · V⁻¹, which suggests that the ZrO₂ layer prevented O₂⁻ ions from transporting to the interface. The thickness of the inner layer in the TEM image is approximately 290 nm and is thicker than that in the SEM image. It can be expected that part of inner layer was dissolved by the KOH solution used for preparation of the samples for SEM analysis. Although the thickness of the Al₂O₃ layer in the ZrO₂-coated foil was thinner, the ZrO₂-coated foils could withstand a voltage of 640 V because of the inner layer including the ZrO₂ layer. Furthermore, the coating layer could withstand the tensile stress caused by volume expansion during the Al₂O₃ formation, which most likely contributed to the formation of the Al–Zr composite material.

Figure 4 presents the TEM–EDS mapping results for the selected area from Fig. 3d. Figure 4a is a TEM image of the selected area, and Figures 4b, 4c, and 4d show the elements distribution of O, Al, and Zr, respectively. Figs. 4c and 4d reveal that the inner layer is divided into two layers, a layer containing mostly Zr atoms and a layer containing mostly Al atoms. Therefore, the total layer formed by the ZrO₂ coating and anodizing was composed of the inner layer, middle layer, and outer layer marked by dashed lines.

Figure 4a presents the EDS line scanning profile obtained from the tunnel of Fig. 4a. The changes in the Al intensity from the inner layer to the outer layer indicated that Al³⁺ ions were transported inwards through the coating layer during anodization. Figure 5b presents EDS spectra from points 1, 2, and 3 marked in Fig. 4a. Al atoms were observed in both the middle layer and inner layer. The Al–Zr composite oxide was formed in the entire ZrO₂ coating layer, and relatively less Al atoms were present in the middle of the layer. The atomic percentages of the elements Zr, Al, and O in points 1, 2, and 3 marked in Fig. 4a are listed in Table I. The atomic ratio of Al to O at point 1 is 2.35, and 5.86 at% Zr was observed. It was demonstrated that many Al³⁺ ions were transported inwards through the coating layer during anodization.
ions were transported through the coating layer during anodization, and most Al atoms existed as aluminum hydrate. The atomic ratio of Zr to O at point 2 is 1.06, which is two times higher than the ratio of ZrO2. This may be due to the inward transport of Zr4+ or ZrO2+ ions under high electric field, as was reported by K. Watanabe, and the loss of O2− ions to the outer layer may also occur. In addition, 3.52% Al atoms were present even in the middle of the ZrO2 layer, which can be considered evidence that the Al3+ ions passed through the coating layer. At point 3, the atomic ratio of Al to O is close to the stoichiometric ratio of Al2O3 (2/3). The lack of O atoms at points 1 and 2 are the most obvious phenomena. Perhaps this is because the dense inner layer and absorbed hydrogen in the inner wall surface prevents the O2− ions from transporting inside.

From EDS analysis results, it was confirmed that the coated and anodized layer could be divided into an inner aluminum hydrate layer, a middle Al-Zr composite layer, and an outer Al2O3 layer. The thicknesses of these layers were approximately 120 nm, 240 nm, and 530 nm, respectively. The results on the etched Al foil were different from those reported on the flat Al foil. It has been observed that the dual-layer structures were formed between the coating layer and flat Al foils. In addition, the coated film on flat Al foils would break off when the anodizing voltage was high. The main reason for these differences was possibly that the coating layer in the etched foil could maintain the round structure under the volume expansion stress of the anodic oxide film during anodizing.

Figure 6 presents HR-TEM images of the coated and anodized foil. The image of the middle ZrO2 layer presented in Fig. 6a reveals that the coating layer was highly densified after being anodized. The inset in Fig. 6a is a magnified lattice image. The measured interplanar spacing, d, is 0.294 nm, which matches with d = 0.29502 nm of the tetragonal ZrO2 (011) crystal plane indexes according to its JCPDF card (card No. 50-1089). In addition, the XRD result of the ZrO2 layer not shown here also matched with the JCPDF card. Figure 6b presents an image of the outer Al2O3 layer. The inset in Fig. 6b is the fast Fourier transform (FFT) image of the Al2O3 layer obtained using Gatan Digital Micro-graph program. The electron diffraction pattern indicates that the outer Al2O3 layer has a crystalline structure. The formation of the crystalline structure may be induced by the higher forming voltage and heat-treatment.

Formation mechanisms of multi-layer film.— Figures 7a and 7b show the variations of anodizing voltage with anodizing time when...
the samples anodized at 600 V with 50 mA/cm² constant currents in the first and second step anodizing. At the initial moment, there are relatively high voltage jumps and they are 110.7 V, 120.5 V for non-coated samples and ZrO₂-coated samples, respectively. The difference of these voltage jumps is caused by the thermal aluminum oxide film. The reasons for the high voltage jumps are not sure, while foils show the lower jumps of voltage when being anodized at lower current density. The different slope of samples with or without coating showed in Fig. 7a is similar to the reported results, while the curve of coated samples shows sudden drop and subsequent raise under the forming voltage. The instantaneous variation of voltage may be explained as follows: The cracks in coating layer are filled with newly formed anodic alumina during anodizing. With the growth of outer Al₂O₃ goes on, the empty space is gradually filled by volume expansion of Al₂O₃ layer. When the compressive stress by the volume expansion is higher than the value that coating layer can stand, the local breakdown may happen in the coating layer where crack exists. After that, it can be repaired by anodizing. However, the anodic oxide layer become stable in the second step anodizing as shown in Fig. 7b. The ZrO₂ coated samples exhibited 26% higher specific capacitance than samples with pure Al₂O₃ layer when being anodized at 600 V.

Figure 8 presents a schematic model of the multi-layer structure formed in the ZrO₂ coated sample before and after anodizing. It is assumed that the ZrO₂ layer has a network structure of micro pores and cracks, which may have been formed by the evaporation of organic compounds during drying and/or annealing. When the coated foil is immersed in anodizing solution, water and electrolyte penetrate into the micro pore network and empty space formed by shrinkage. During the initial stage of anodizing, the transport of Al³⁺, O²⁻, or OH⁻ through the micro pores was not difficult. The Al₂O₃ layer was formed between the coating layer and Al substrate by outward transport of O²⁻ or OH⁻ ions dissociated from water. The Al³⁺ ions were transported inward form the aluminum oxide and filled the micro pores in the coating layer. As the Al₂O₃ layer grew in the empty space, the tensile stress caused by the volume expansion of aluminum oxide increased. Thus, the newly formed aluminum oxide compressed the ZrO₂ coating layer, and the coating layer was gradually densified.

Conclusions

ZrO₂ thin films were successfully coated on etched foil using the vacuum infiltration method. The thickness of the 4 times coating layer was approximately 110 nm. A multi-layer structure (inner aluminum hydrate layer, middle Al-Zr composite layer, and outer Al₂O₃ layer) is formed in the ZrO₂-coated sample before and after being anodized at 600 V. The thicknesses of these layers were approximately 120 nm, 240 nm, and 530 nm, respectively. This phenomenon differs from the formation behavior of composite oxide films on flat Al foils. Although the thickness of the Al₂O₃ layer anodized in the ZrO₂-coated foil was thinner than that of the non-coated Al foils, the ZrO₂-coated foils could withstand a voltage of 640 V because of the inner layer including the ZrO₂ layer. Al atoms existed in the inner layer, and the entire coating layer transformed into the composite film. The volume expansion of the outer layer during anodizing was helpful for transporting the Al atoms and forming the Al-Zr composite layer. The ZrO₂ coated samples revealed 26% higher specific capacitance than samples without coating, which suggests that the vacuum infiltration and anodizing method is an effective way to increase capacitance of anodized aluminum foils.

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