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# Analysis of Polymer Hybrid-coated Anodic Aluminum Oxide

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*Aluminum (Al) is a lightweight, thermally high conductive, reflective and non-toxic metal that can be easily machined. However, weak corrosion and wear resistant of Al, comparing to other metals are limited to apply it to a heat transfer plate. In order to overcome these drawbacks, anodic oxidation method has been applied to produce anodic Al oxide (AAO) and then the AAO sheet is then immersed into the nano-hybrid solution. The properties of obtained samples were evaluated. It was found that the modified Al anodizing one could produce a hard oxide coating with good corrosion protection and thermal conductivity.*

**Keywords** Heat transfer plate; Anodic aluminum oxide; Corrosion protection; Thermal conductivity

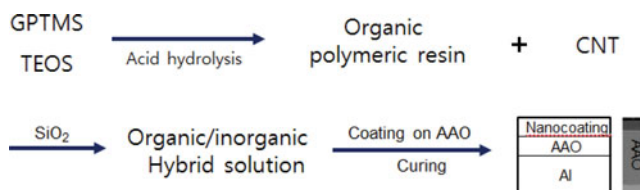
## Introduction

The heat transfer plates are mainly made of copper, titanium (Ti) or stainless steel at present. To reduce usage of these materials in heat exchanger industry, manufacturers have started to use aluminum (Al) as a substitute to product the heat transfer plate due to its high thermal conductivity, abundant resources and lower price (lower by one third of the copper price) [1,2]. However, in many instances inadequate corrosion properties and low surface hardness have greatly restricted the application of Al [3]. Anodic aluminum oxide (AAO) hold good prospect for various industrial applications due to their unique properties such as well ordered porous structure [4]. However, the porous oxide surface is easily to be penetrated by  $\text{Cl}^-$  ions in seawater, so it limits the industrial application in marine environment [5,6].

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**Figure 1.** Preparation of nano-coated AAO sheet.

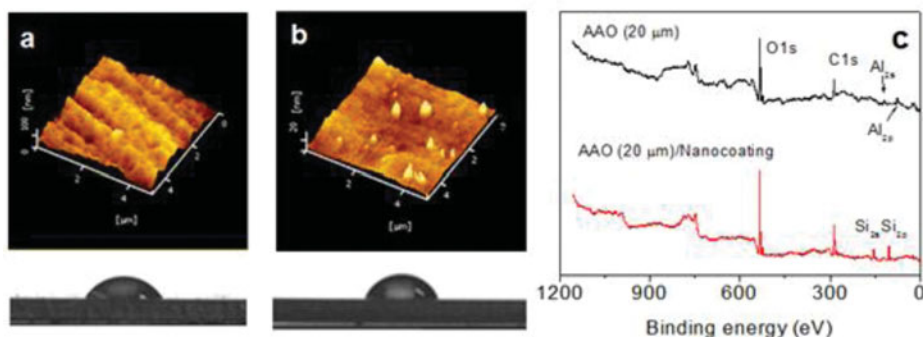
Thus, the production of hard, corrosion resistant coatings on aluminum components is of great interest.

Surface modification or functionalization of AAO film can be expected to significantly widen application scopes. Polymer-modified AAO films have shown improved binding capacity, selectivity, biocompatibility, and lubricating properties in comparison to non-modified AAO films [7]. In this study, Al sheet was anodized to increase the corrosion resistance and surface hardness. However, polypores produced by anodization generate make it poor corrosion properties. To enhance these properties, a sealing of porous morphology was conducted by sol-gel hybrid coating. The properties of coated AAO sheet were evaluated by scanning electron microscopy and contact angle measurements and for corrosion, the slat spread tests of nano-coated sheets were carried out in 5% NaCl fog at 35°C.

## Experimental

The aluminum samples with a purity of 99.9% were used. Anodic oxidation of Al sheet was carried out in 30 vol% H<sub>2</sub>SO<sub>4</sub> solution. The temperature was kept at 7°C under continuous stirring. A thickness of anodization layer was controlled by oxidation time under a current density of 3 A/dm<sup>2</sup> (10, 20, 30 μm). After forming the oxide film by the anodic oxidation, the samples were rinsed and dried. To improve corrosion resistance, the AAO sheet was sealed by the sol-gel method. The organosiloxane solution was prepared by combining ((3-glycidoxo propyl)trimethoxy silane) (GPTMS), tetra orthosilicate (TEOS), and acetic acid in a 1:1.7:1 weight ratios and stirring for 3 hrs at 90°C and then carbon nanotube was added. After the hydrolysis, the viscosity was controlled by adding a solvent. SiO<sub>2</sub> nanoparticles were added and mixed with stirring for 24 hrs and the sol-gel nanocoating on AAO was conducted by dipping into the solution (Figure 1).

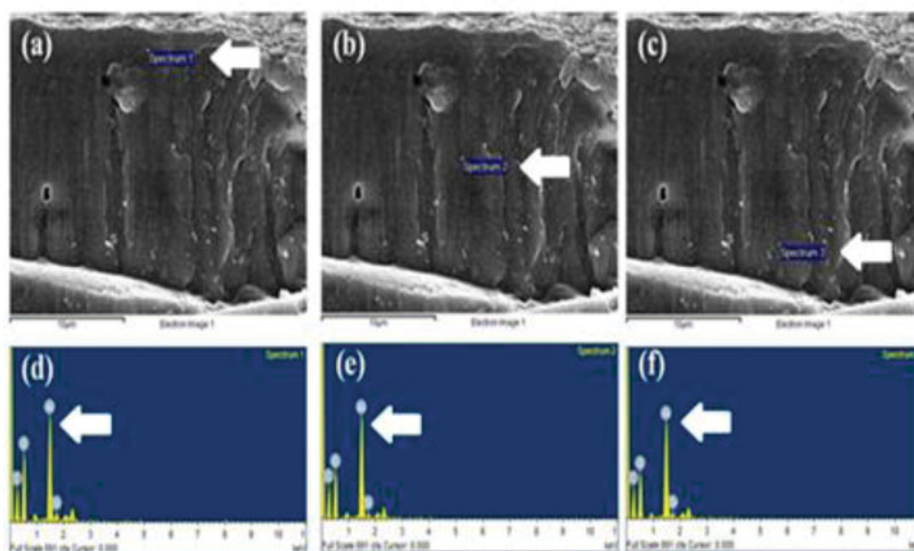
Surface atomic mapping image was obtained on a JEOL JSM-6100 scanning electron microscope (SEM). An energy dispersive X-ray spectrum was also used. The static contact angle of water onto the surface of samples was measured using a Kruss contact angle meter. The surface chemical compositions were obtained using Perkin-Elmer Physical Electronics Model 5300 ESCA. ESCA measurements were performed with MgKα X-ray source at 15 kV and 20 mA. The corrosion resistance of samples was measured by a salt spray tester where 5% NaCl solution is continuously spread in a chamber at 35°C. The thermal conductivity and diffusivity of sample (Diameter: 12.5 mm and Thickness: 1 mm) was measured by using LAF 457 micro flash. Samples were prepared in disc-shaped one with diameter of 12.5 mm and thickness of 1 mm.



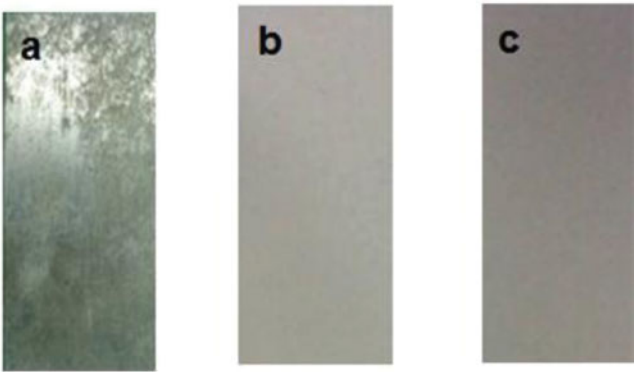
**Figure 2.** AFM images of AAO (a) and nano-coated AAO (20 μm) (b) sheets and their ESCA survey spectra (c). The bottom images of a and b correspond to their contact angle images to water.

## Results and Discussion

Aluminum (Al) is a highly reactive material and its anodization could improve the durability and the resistance to corrosion. However, the anodizing of Al produces porous structure which leads great chemical activity due to high surface area. To enhance property, a sealing of porous morphology is required [4,6,7]. Figure 2a and 2b show surface images of AAO and nano-coated AAO sheets measured by AFM. The anodizing sheet showed porous morphology due to oxidation. After the sealing process by sol-gel method (nanocoating), the sheet surface became smooth (surface roughness  $R_a$  is decreased to 0.2 μm). Two small peaks in low binding energy in ESCA survey spectra were newly observed (Figure 2c). These peaks correspond to Si 2p and Si 2s of silica. Also, contact angle to water increased from 62° to 76° after the hydrophobic nanocoating.



**Figure 3.** SEM images of fractured nano-coated AAO (20 μm) sheets at different positions. The arrows indicate the measured position and Si peak.



**Figure 4.** Visual test of AAO (10  $\mu\text{m}$ ) (a), nano-coated AAO (10  $\mu\text{m}$ ) (b), and nano-coated AAO (30  $\mu\text{m}$ ) (c) after 500 and 2200, and 2200 hrs, respectively, in a salt fog chamber.

Since surface morphology, and contact angle, and ESCA data provide information on surface coating on AAO, the fracture plane of sheets was measured. Figure 3 show SEM images and their EDX results of nano-coated AAO sheets according to a position in the fractured AAO layer. Silica concentrations of ca.1.5 wt% were observed, regardless of the position. These results indicate that the pores were well sealed by the silica particles.

Visual tests have also been performed on AAO and nano-coated AAO sheets. Figure 4 shows the salt fog data of samples. For Al, pitting corrosion is most commonly produced by halide ions. It is evident that the nano-coated AAO sheets shows significantly improved corrosion resistance. After 500 hrs in a salt fog chamber, the pitting corrosion was observed in the AAO sheet. However, there was no morphological change in the nano-coated AAO sheet after 2200 hrs exposure. Anodizing and sealing of Al improve resistance to corrosion. For heat transfer plate, the thermal conductivity (K) of materials is an important factor. K in this study was obtained by using the following general relationship from the corrected thermal diffusivity [8].

$$K = \alpha \times C_p \times \rho \tag{1}$$

where K is the thermal conductivity,  $\alpha$  is the thermal diffusivity,  $\rho$  is the density, and  $C_p$  is the specific heat.

**Table 1.** Thermal conductivities of nanocoated AAO sheet

Sample	Layer	Thickness (mm)	Thermal conductivity (W/m·K)	Total thermal conductivity (W/m·K)
Nanocoated AAO (10 $\mu\text{m}$ )	Al	0.979	142.839	25
	Modified layer	0.025	0.75	
Nanocoated AAO (20 $\mu\text{m}$ )	Al	0.785	142.839	12.673
	Modified layer	0.045	0.75	
Nanocoated AAO (30 $\mu\text{m}$ )	Al	0.754	142.839	8.791
	Modified layer	0.066	0.75	

Table 1 shows the thermal conductivities of nano-coated AAO sheets as a function of AAO thickness. A thermal conductivity of double layers, Al (A) and nano-coated AAO (B), was calculated by the following eq.

$$K_{AB} = 1/(T_A/T_{A+B}/K_A + T_B/T_{A+B}/K_B) \quad (2)$$

where K is the thermal conductivity and T is thickness of layer. The results showed that the thermal conductivity is rapidly decreased by increasing AAO thickness due to the poor thermal conductivity of porous AAO. However, the thermal conductivity of nano-coated AAO (10  $\mu\text{m}$ ) sheet, 25 w/mK was enough to be used for heat transfer plate if we consider the thermal conductivities of Ti and stainless steel are 16 and 15 w/mK, respectively.

## Conclusion

In conclusion, hydrophobic and hard surface on aluminum is successfully generated by anodization process and physical sealing. The anodization of Al improved the mechanical property, except corrosion resistance due to their porous structure. To seal the pores, the hybrid coating prepared by sol-gel method was conducted by dip process. The hybrid-coated AAO sheet showed good corrosion resistance. Although a thermal conductivity of AAO sheet is rapidly decreased with AAO thickness, Al sheet with 10  $\mu\text{m}$  AAO shows good corrosion resistance and thermal conductivity for application in heat transfer plate.

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