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A Study on Formation of Anodic Oxidation Film on Type 60 Aluminum Alloy Followed by Difference of Pretreatment

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Abstract

The purpose of this study is to check the influence of difference of pretreatment in anodizing in aluminum alloy on formation of anodic oxide film (AAO). AL type 60 alloy was used for material and Sodium Hydroxide (NaOH) etching along with desmutt, chemical polishing and electrolytic polishing were performed. Anodizing was performed in preprocessed and non-preprocessed state in identical condition of 3 each electrolytes. Specimen was measured with optical microscope. As result, it was found that there was difference of form of generated anodic oxide film.

Keywords: pretreatment, chemical polishing, electrolytic polishing, aluminum alloy, anodic oxidation film

1 Introduction

Anodizing uses aluminum and its alloy to manufacture alumina (Al_2O_3) oxide film with evenly arrayed fine pores vertical to the surface in which active studies are in progress in various fields.[1]~[5] Also, it is well known by preceding researchers that characteristic of oxide film generated by anodizing aluminum or its alloy substantially varies depending on composition of electrolyte solution and anodizing condition.[6]~[9] Anodizing can be classified into static voltage method and static current method depending on method of electricity supply. Adjustment of fine pore size, distance between pores, and thickness of barrier is convenient when anodizing by static voltage and control of porous layer thickness is convenient when anodizing by static current.[10] Thus, pore size of oxide layers is proportionate to the applied voltage and porous layer thickness of oxide layers is proportionate to current.[11] State of aluminum material surface is very important to gain evenly arrayed porous layers using anodizing. When anodizing with aluminum material that has irregular surface, the shape of pores are irregularly generated. Therefore, aluminum alloy surface must be maximally made flat through various pretreatment in order to gain porous layer with regular arrays through anodizing.

Aluminum 60 type alloy is used in this study to perform anodizing to manufacture porous layer. Various pretreatment methods were conducted to improve roughness of the aluminum alloy plate surface. Meanwhile, procedure omitting pretreatment was performed to generate anodic oxide film which become the target of comparison. 3 types of electrolytes were used to check if forms of each oxide film were different.

2 Experiment

Flatness of aluminum alloy surface is important when manufacturing anodic oxide film of aluminum alloy in even form. Therefore to investigate the influence of aluminum alloy surface state on the porous layer that is generate by anodizing, aluminum alloy with flat surface by pretreatment and aluminum alloy without pretreatment were used for constant voltage anodizing. Through this, the influence of material surface state on formation of porous layer was studied.

Figure 1 is the anodizing process chart of AL 6061 aluminum alloy. After pretreatment of anodizing on aluminum alloy such as mechanic polishing, etching, desmutt, chemical polishing, and electrolytic polishing, the aluminum alloy surface was cleanly washed for anodizing. For mechanical polishing, paper polishing (#80, #220, #600, #1500 order) was first performed in a polishing machine to remove relatively large particles and mirror polishing was performed with 1 ㎛ alumina polishing liquid. Afterwards for flattening of surface and removal of naturally formed oxide film in the air, chemical polishing was performed for 10 min in 80 ℃ in 3.5 Vol% H_3P0_4 and 45g/L CrO_3 mixed solution. Lastly, electrolytic polishing was performed with 1A current for 15 min in 40 ℃ in H_3P0_4 : H_2SO_4 : H_2O (7 : 2 : 1) solution. AL 6061 was used for anodizing material. Composition of material is shown in Table 1.

Figure 2 is the Schematic diagram of apparatus for aluminum anodic oxidation. After setting type, concentration, and temperature of electrolytes, AL 6061 alloy specimen was attached on the anode of DC power supplier and AL 1050 on the cathode to connect power. Here, 3 types of electrolytes, 15 wt% H_2SO_4, 0.3M $(COOH)_2{\cdot}2H_2O$, and 2M H_3PO_4 were used for anodizing-use electrolytes and temperature of 20 ℃ was maintained. Static voltage of 20 V was applied in H_2SO_4 and 100 V was applied in $(COOH)_2{\cdot}2H_2O$ and 2M H_3PO_4. In addition, in order to observe the morphology of the pores that were generated when the voltage was changed, the anodic oxidation was carried out by 40V and 100 V. Air was supplied in electrolytes during anodizing for air agitation.

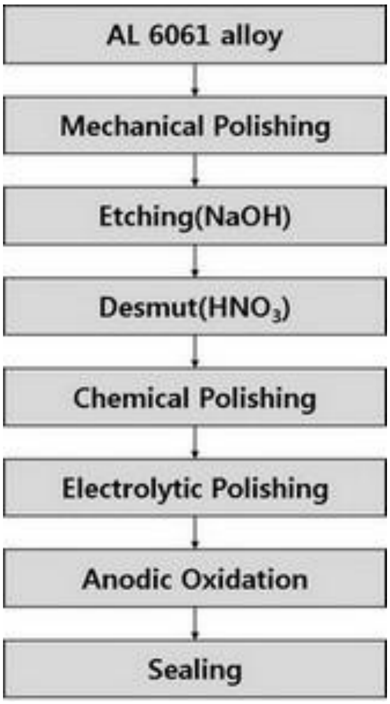


Fig. 1. Flowchart of Al 6061 anodic oxidation process

Table 1. The composition of the aluminum 6061 alloy

	Al	Mg	Si	Fe	Cu	Mn	Cr	Zn	Ti
6061	95.8~98.6	0.8~1.2	0.4~0.8	Max 0.7	0.15~0.4	Max 0.15	0.04 ~ 0.35.	Max 0.25	Max 0.15

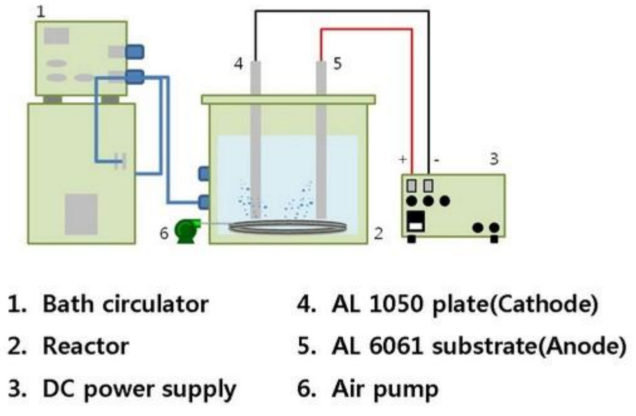


Fig. 2. Schematic diagram of apparatus for aluminum anodic oxidation

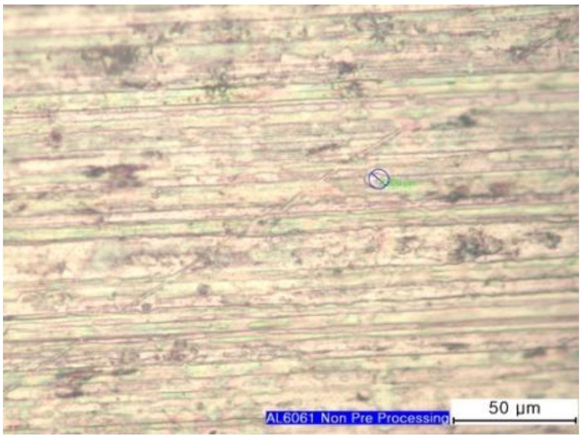
3 Results and Consideration

Anodizing was performed using flattening preprocessed material of AL 6061 alloy surface and material without pretreatment, and influence of aluminum alloy surface state on formation of anodic oxide film was observed.

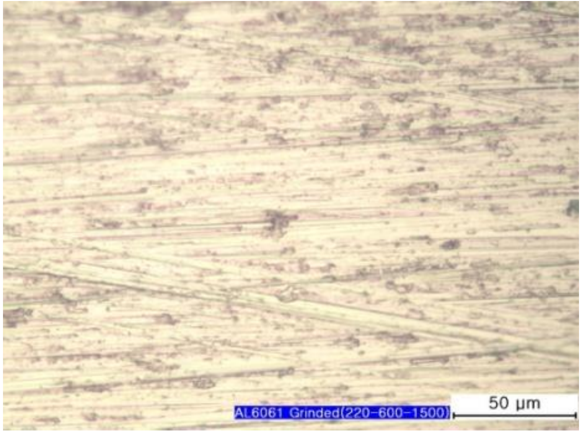
Figure 3 is a picture of observed surface state of aluminum alloy material in each step from the polishing process to the electrolytic polishing process. Figure 3 (a) is a 500 times enlarged picture of the rough rolling material alloy plate with flaws. Figure 3 (b) is a 500 times enlarged picture after mechanical polishing on the material in Figure 3 (a). The deep processing line that occurred during rolling became very soft and large flaws were removed in which partial flaws remained. If anodizing is performed in state with many flaws, ion concentration occurs in flawed parts in which even distribution of pores is difficult to achieve.

Figure 3 (c) is a 500 times enlarged picture after performing etching for 30 sec in 70 ℃ in NaOH solution in which partial flaws remained in the surface but most processing lines disappeared. Figure (d) shows that the picture became slightly brighter after performing desmutt. It is seen that smut components that were generated by dissolution from alloy during etching were washed off.

Figure (e) is a 500 times enlarged picture after performing chemical polishing in which naturally generated oxide film was removed with better surface roughness to show cleaner results compared to Figure 3 (d). Electrolytic polishing in Figure (f) is the process making better roughness by melting aluminum alloy surface with acid as thin alumina (Al_2O_3) film of fine pores was formed to have similar form after anodizing. This is because the same effect of anodizing was shown.

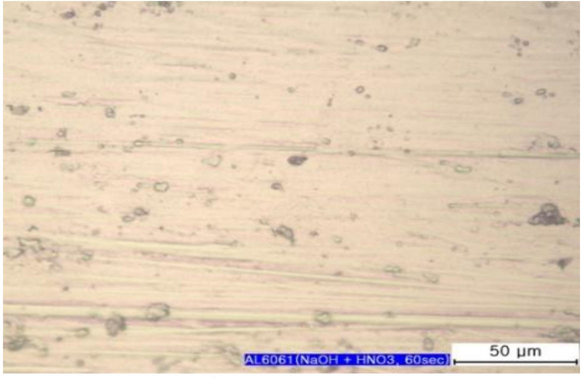


(a) Original AL 6061 material

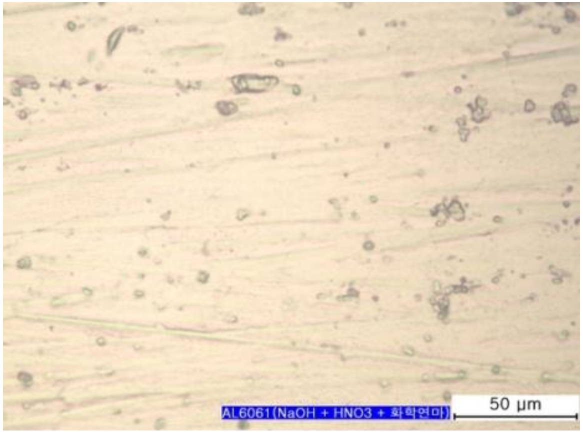


(b) After mechanical polishing

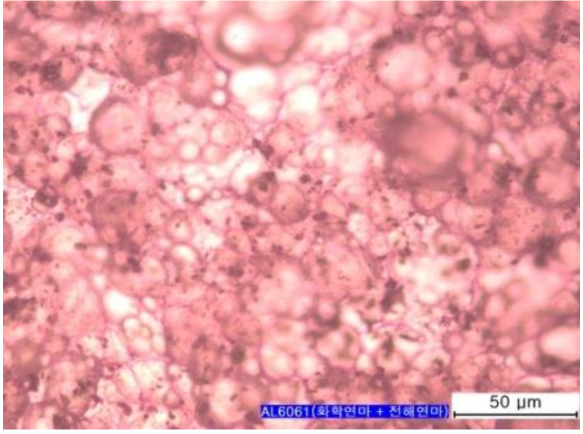
(c) After etching (NaOH)



(d) After desmutt (HNO_3)



(e) After chemical polishing

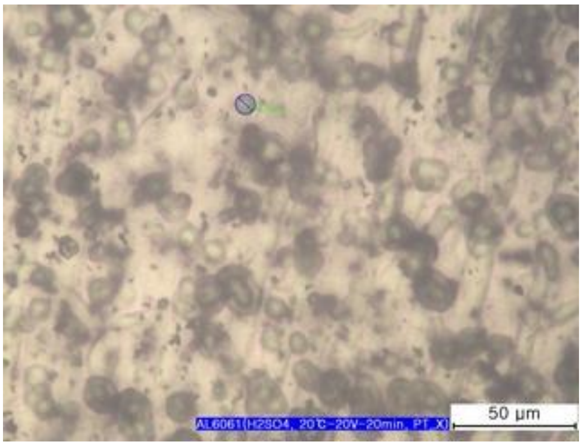


(f) After electrolytic polishing

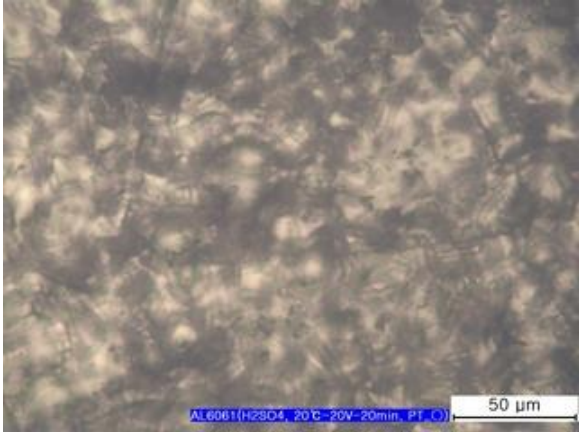
Fig. 3. Variation of the aluminum surface due to pretreatment process

Figure 4 is a picture of aluminum alloy specimen with and without pretreatment showing comparison of anodized results. Figure 4 (a) and 4 (b) is the is the surface image after anodizing in sulfuric acid (H_2SO_4) solution and Figure 4 (c) and 4 (d) is the surface image after anodizing in oxalic acid ($(COOH)_2{\cdot}2H_2O$) solution. Irregular surface can be seen in specimen without pretreatment. On the other hand, the anodized specimens with clean surface by pretreatment show comparatively even arrayed pores.

Meanwhile, size of oxide film formed during anodizing can be controlled by adjusting voltage.[5] Size of pores increases when increasing applied voltage. However, type and concentration of electrolyte must be changed when generating pores with size of hundreds nanometer. This is because current increases proportionate to higher applied voltage in which very high current flow can rapidly increase electrolyte solution temperature. Therefore, type and concentration of electrolyte must be changed to stabilize current.[5] It could be seen in sulfuric acid (H_2SO_4) solution that rapid heating occurs when applied voltage instantly exceeds 25 V as current exceeding the rectifier flows.

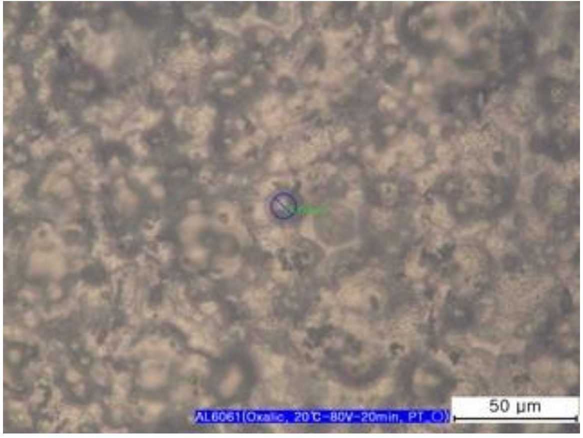


(a) without pretreatment (Sulfuric acid)



(b) with pretreatment (Sulfuric acid)

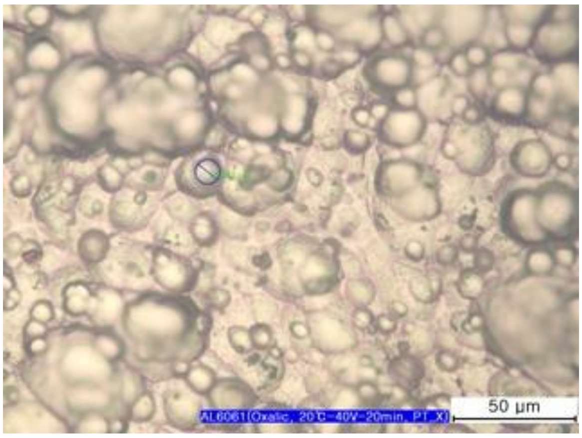
(c) without pretreatment (Oxalic acid)



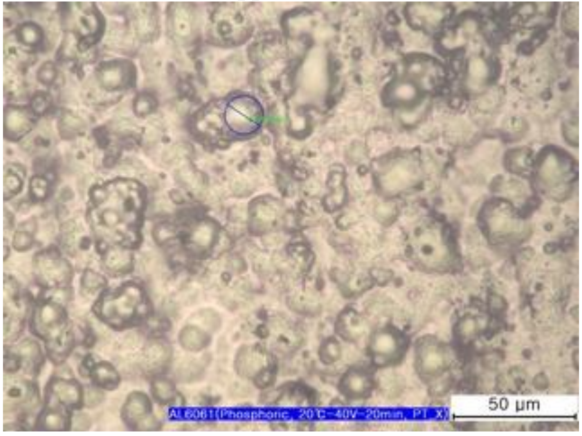
(d) with pretreatment (Oxalic acid)

Fig. 4. Form of surfaces after anodic oxidation according to the pretreatment presence

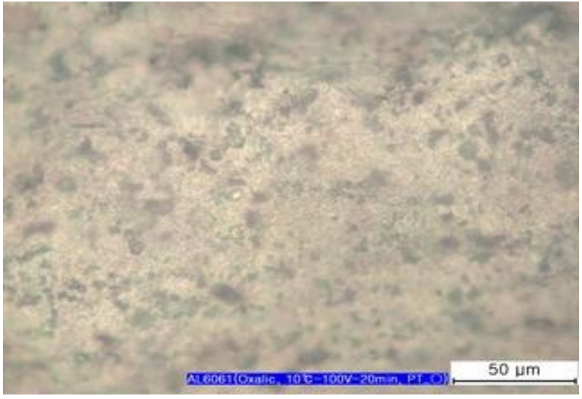
Figure 5 shows difference of generated pores in oxalic acid ($(COOH)_2 \cdot 2H_2O$) and phosphoric acid (H_3PO_4) solution when changing applied voltage during anodizing. Figure 5 (a) and 5 (b) are enlarged shapes of formed surface after anodizing for 20 min in each 40 V and 100 V in oxalic acid ($(COOH)_2 \cdot 2H_2O$) solution and Figure 5 (c) and 5 (d) are enlarged shapes of formed surface after anodizing for 20 min in each 40 V and 100 V in phosphorous acid (H_3PO_4) solution. Comparing anodic oxide films in each 3 electrolytes, film thickness generated in sulfuric acid was most thick and oxalic acid, phosphorous acid followed in order. However, thickness of generated film in oxalic acid and phosphorous acid were too thick for accurate measurement. It was known from the results of this experiment that electrical conductivity of sulfuric acid electrolytes was most outstanding and heating excessively occurred in sulfuric acid solution when exceeding applied voltage of 25 V in which smell of burning occurs in both poles. It was known that performing anodizing in sulfuric acid solution was more dangerous than oxalic acid or phosphorous acid.



(a) 40V applied (Oxalic acid)



(b) 100V applied (Oxalic acid)



(a) 40V applied (Phosphoric acid)

(b) 100V applied (Phosphoric acid)

Fig. 5. Surface change by applied voltage

4 Conclusion

Alumina inductor which is anodic oxide film generated by anodizing generates fine porous layers of nanometer size. Necessity of pretreatment can occur when manufacturing this kind of fine porous layer depending on aluminum alloy surface state. The results of flattening pretreatment and anodizing experiment of aluminum alloy surface are summarized as follow.

1. Before anodizing, pretreatment must be performed to make aluminum alloy plate surface flat in order to gain evenly arrayed fine anodic oxide film porous layers.
2. Mechanical polishing is a physical surface reforming process in which maintaining identical condition is significant. Constantly maintaining chemical composition ratio, temperature, and time is important in chemical polishing and electrolytic polishing procedures because as they are chemical/electrochemical surface reforming methods.
3. Mechanical polishing, etching (removing), desmutt, chemical polishing, and electrolytic polishing were formed for pretreatment.
4. When performing anodizing with 20 V static voltage in sulfuric acid (H_2SO_4) electrolyte using surface flattened aluminum alloy plate by pretreatment, formation of even porous layer was found compared to specimen without pretreatment.
5. If the applied voltage is large, the heat value of electrolytic solution and anode can be increased while the current value is increase. Therefore if the applied voltage is less than 20V we should use sulfuric acid and more than 20 V we need to use Oxalic acid or Phosphoric acid. By doing so, it is necessary to prevent rapid rising of the amount of current even though applied voltage is raised.
6. Manufactured template with fine pores can be used in various sensors, mass storage devices, and display devices.

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