



## Effect of Current Density on Porous Film Formation in Two-Step Anodizing for Al Alloy

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### Abstract

Anodizing is a technology to generate thicker and high-quality films than natural oxide films by treating metals via electrochemical methods. Electrochemical manufacturing method of nano structure is an efficient technology in terms of cost reduction, high productivity and complicated shapes, which receives the spotlight in diverse areas. Especially, artificial films generated by anodizing technology possess excellent mechanical characteristics including hardness and wear resistance. It is also easy to modify thickness and adjust shape of those artificial films so that they are mainly used in sensors, filters, optical films and electrolytic condensers. In this study, experiment was performed to observe the effect of current density on porous film formation in two-step anodizing for Al alloy. Anodizing process was performed with 10 vol.% sulfuric acid electrolyte while the temperature was maintained at 10°C using a double beaker, and 10 ~ 30 mA/cm<sup>2</sup> was applied for 40 minutes using a galvanostatic method. As a result, both pore diameters and distances between pores tended to increase as the local temperature and electrolysis activity increased due to the increase in applied current density.

*Keywords : Anodizing, Oxide films, Nano structure, Current density*

### 1. Introduction

Generally, the purpose of surface modification is to improve corrosion protection, wear resistance, exterior appearance of substrate by generating a protective films using physical and chemical treatment methods on the surface of metallic materials. Among the surface modification techniques, anodizing is an emerging technique for it not only meets the purpose like these, but also has the advantage of its low price [1]. Films generated by anodizing is largely divided into porous film and barrier film. Especially, an acid electrolyte forms porous structure by dissolution reaction of anodized film generated in the early stage [2]. These pores generated by the

above process can be adjusted with treatment processes; especially, porous structure generated via two-step anodizing process has a uniform size of pores in regular arrangement [3]. With emergence in nano technology, researchers have been attempting to generate nano structure oxide on various materials including Al, Zr, W, and Ti [4]. Especially, steady research is conducted on aluminum, one of the most important and indispensable materials in modern industry, with constantly increasing demand. In related studies, Moon et al. [1] observed anodized film formation behavior of Al 7075 alloy in sulfuric acid, and Son [5] studied the effect of equal channel angular pressing (ECAP) depending on pitting corrosion resistance of hard anodized Al 5052 alloy. In addition, Kang et al. [6] sealed Al alloy using nano diamond powder after anodizing using oxalic acid to improve corrosion and wear resistance. Therefore, this study proposes to select the optimum aluminum anodizing condition to perform excellent

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corrosion resistance and durability in the harsh marine environment upon generating porous film with current density in sulfuric acid.

## 2. Experimental Details

In this study, to produce a uniform porous coating of the 5083 aluminum alloy, electro-polishing was performed for 3 minutes under the conditions of 25 V and 5°C with a mixture solution of ethanol (95%) and perchloric acid (70%) at the volume ratio of 4 : 1. Then, first-step surface modification was performed with 10 vol.% sulfuric acid electrolyte while the temperature was maintained at 10°C using a double beaker. For the anode, a 5083 aluminum alloy with a 5 mm thickness and a size of 2 × 2 cm was used, and for the cathode, a platinum electrode was used, with a fixed distance of 3 cm between the two electrodes. During the surface modification, the solution was agitated at a constant speed for the stable growth of the oxidation layer due to increasing local temperature, and 10~30 mA/cm<sup>2</sup> was applied for 40 minutes using a galvanostatic method. After that, the irregular oxidation coating generated from the first step surface modification was removed, and for the second step surface modification process (same as first step), etching was performed with a mixed solution of chromic acid (1.8 wt.%) and phosphoric acid (6 wt.%) at 60°C for 30 minutes. After surface modification, the pore structure and porosity were observed with a field emission scanning electron microscope (FE-SEM) and 3D analysis microscope. And composition and types of crystal material on the surface was analyzed by using X-ray diffraction (XRD). Additionally, the chemical compositions of the specimen are shown in Table 1.

## 3. Results and discussions

Figure 1 depicts the observation of surface morphology and porosity after anodizing in 10 vol.% electrolyte at 10°C and 40 minutes of processing time with current density. Thompson et al. [7] claimed that porous layers would develop when reached the state of equilibrium for formation of oxide layer between aluminum substrate and barrier layer, and dissolution reaction between barrier layer and

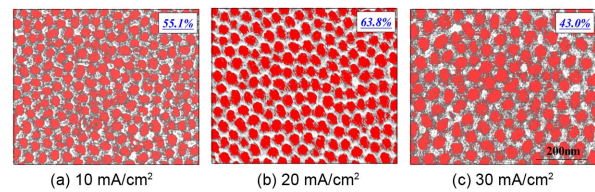


Fig. 1. Analysis of the porosity of anodized Al samples with different current densities.

electrolyte. At the early stage of formation of porous films through anodizing, small pores are generated on the aluminum surface while current is concentrated. With exothermic reaction from the formation of porous films, electrochemical dissolution reaction becomes more active that results in the growth of pores. In order for pores to develop into a structure with uniform density and size, the initial surface must be smooth. Otherwise, uneven dissolution reaction is generated by natural oxide films and roughness of aluminum itself [8]; we conducted electro-polishing to obtain leveled and clean surfaces before anodizing. As the result of experiment, small and irregular formation of pores was observed at 10 mA/cm<sup>2</sup> whereas hexagonal structure that is unique to aluminum was formed along with relatively clear and fine barrier layer at 20 mA/cm<sup>2</sup>. On the other hand, irregular structure with extremely large pores was observed at 30 mA/cm<sup>2</sup>. Especially, fine porosity expanding to the surface of substrate existed within the pores in all conditions [2]. According to Michelson [9], pores would grow again if the thickness of barrier layer is thinned enough to generated field assisted dissolution. Electric field is formed at the time of field assisted dissolution and pores develop in all directions by this distribution [10]. Pure aluminum, in addition, generates almost uniform films; however, current is partially concentrated in an alloy by the existing metals with different conductivity. As a result, conical asperity was observed downwards in the pores [11]. Especially, a high contents of Si has low film generation rate so that it is necessary to refine particles through proper heat treatment. Overall the pore diameter tended to grow as the current density increased. As can be seen in the process of pore formation, thickness of films decreased due to the destruction of barrier layer by an anion in the early stage of reaction. As a result,

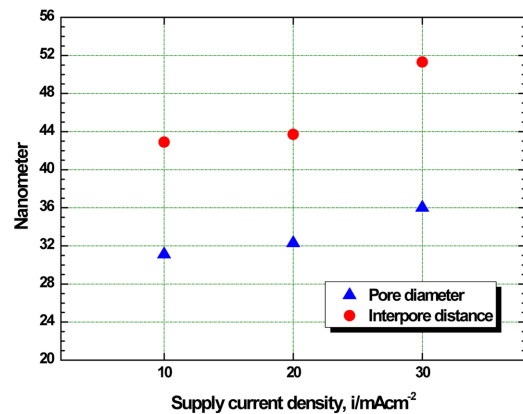
Table 1. Chemical composition of Al alloy

Components(wt.%)	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
	0.40	0.15	0.18	0.18	6.42	0.12	0.04	0.01	Bal.

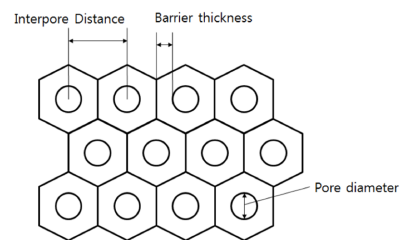
current concentration phenomenon occurred, which led to increase in temperature. Therefore, increase in temperature on such surface led to heightened activity of electrolyte, which resulted in large formation of pore diameters with active dissolution reaction [8]. In porosity rate, 55.1%, 63.8% and 43.0% was presented at the current density of 10 mA/cm<sup>2</sup>, 20 mA/cm<sup>2</sup> and 30 mA/cm<sup>2</sup> respectively. Irregular formation was observed at the current density of 10 mA/cm<sup>2</sup> due to the unstable development of pores. The highest porosity rate was yielded at 20 mA/cm<sup>2</sup> as the thickness of barrier layer was thinned a little with a uniform pores.

Figure 2 presents the measurement of pore diameters and interpore distance after anodizing for 10 vol.% electrolyte at 10°C and 40 minutes of processing time with current density. At 30 mA/cm<sup>2</sup>, pore diameter was greater and barrier layer was thicker than those at other condition. Pore diameters of 31.1 nm, 32.3 nm and 36.0 nm were yielded at current density of 10 mA/cm<sup>2</sup>, 20 mA/cm<sup>2</sup> and 30 mA/cm<sup>2</sup> respectively, which tended to increase in proportion to the increase of current density. Interpore distances exhibited 42.9 nm, 43.7 nm and 51.3 nm respectively. As a result, pore diameters and interpore distances were grew as the current density increased. Especially, pore diameters and interpore distance increased as the current density shifted from 20 mA/cm<sup>2</sup> to 30 mA/cm<sup>2</sup>. However, those values remained about the same for the current density of 10 mA/cm<sup>2</sup> and 20 mA/cm<sup>2</sup>. It is determined that barrier layer around pores was dissolved and reamed as the film generated at low current density was exposed to the electrolyte for a long time resulting in long reaction time. In addition, uniform structure was not formed in the case of the applied current density of 30 mA/cm<sup>2</sup> as the surface was damaged due to rapid oxidation reaction and extreme increase in dissolution reaction of film by the electrolyte at the same time. The largest pore diameter was observed at 30 mA/cm<sup>2</sup> among the three anodizing conditions. As the current density increases under the same condition, activity of electrolyte piled up due to the increase in the amount of concentrated current and temperature [8].

Figure 3 shows XRD analysis results that investigated crystal surface structure after anodizing for 10 vol.% electrolyte at 10°C and 40 minutes of processing time with current density. Peak value was presented only 38°, 44°, 64° and 77° while no  $\alpha$  or  $\gamma$ -alumina was observed. Only the pure parent aluminum peak was observed in all conditions. According to previous



(a) Pore diameter and interpore distance



(b) Schematic diagram of surface analysis

Fig. 2. Surface analysis after anodizing process with applied current density.

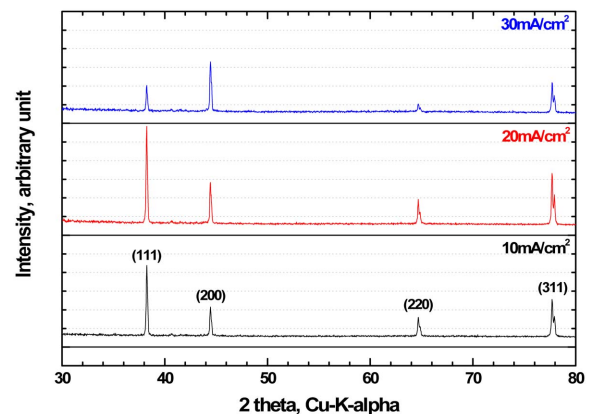


Fig. 3. XRD spectra after anodizing process with applied current density.

studies, oxide film in amorphous structure was generated in anodizing without hydration treatment on aluminum specimen [12]. Likewise, aluminum peak was observed only in this study so that amorphous anodized film was formed. Oxide film generated on the surface was amorphous  $\gamma$ -alumina with vertical pores on the surface and its hardness and wear resistance are known to be excellent with outstanding adhesion to substrate. As the voltage increases, time for constant voltage to reach continues and constant current flows in aluminum continuously. This creates strong electric field

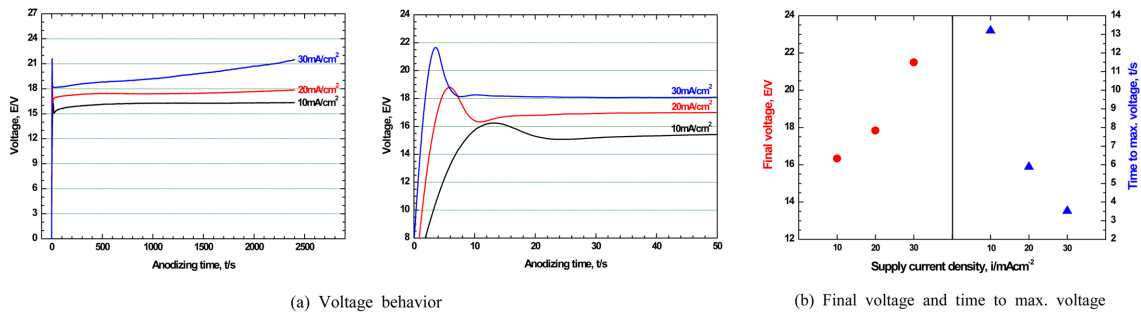


Fig. 4. Electrolysis voltage analysis for anodizing process with applied current density.

between the base material and film with heat. Such heating effect increases driving force to change the shape of film [13]. In this study, low voltage and short processing time did not cause any amorphous change in oxide films.

Figure 4 exhibits voltage measurement results after anodizing for 10 vol.% electrolyte at 10°C and 40 minutes of processing time with current density. As a result of observation on voltage behavior in Fig. 4(a), electrolysis voltage rapidly increased in the early stage to reach its maximum with processing time, gradually decreased and stabilized after certain time. As current density increased, the maximum electrolysis voltage increased and the time to reach the maximum electrolysis voltage tended to shorten. While anodizing aluminum,  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  were combined to form  $\text{Al}_2\text{O}_3$  and partial dissolution reaction was generated between the electrolyte and the surface of substrate to asperate the surface. Electric field, then, was concentrated on the thin part of film that dissolves the film and form pores. In other words, pores started to generate as the film was thicker than a certain value. When pores were formed on the surface through such process, voltage exhibited stable behavior [14]. Especially, almost uniform electrolysis voltage was maintained until the end of the experiment at 10 mA/cm<sup>2</sup>; however, voltage greatly increased towards the end of anodizing as the applied current density increased. This signifies the thickness of films increased as oxidation reaction progressed. Moreover, the higher the electrolysis voltage, the thicker the film developed. As the thickness of films increased, transference of anions through pores slowed down that resulted in the decrease in the generation rate of films. Electric field was not formed at the bottom of pores due to  $\text{Al}_2\text{O}_3$  film, a non-conductor so that chemical dissolution rate by the electrolyte increased. Thus, the thickness of films from anodizing remained almost constant. As the

current density increased, the electrochemical dissolution reaction ( $\text{Al}_2\text{O}_3 + 6\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O}$ ) was suppressed to increase the hardness, wear resistance and marginal thickness of the film [15]. Such thickness of films theoretically increases according to Faraday's law which is linearly proportional to electrolysis time under a constant current density; however, it may deviate from the law depending on the dissolution reaction of electrolyte. The final electrolysis voltage increased from 16.6 V (10 mA/cm<sup>2</sup>) to 17.8 V (20 mA/cm<sup>2</sup>), then 21.5 V (30 mA/cm<sup>2</sup>) as compared in Fig. 4(b) with higher current density. Many scholars share such view in which pore diameters change due to the difference in voltages. Keller et al. [9] claimed pore diameters were irrelevant to voltage, but Wood, Neufeld, and Park et. al. [16] have verified pore diameters increased with an increase in voltage. In addition, Lee et al. [17], the pore diameters were independent to voltage, however, becomes large according to the increasing voltage at high voltage. Electrolysis voltage heightened with an increase the current density, resulting in high solvency and forming larger pores in shorter time (13.2 s for 10 mA/cm<sup>2</sup>, 5.9 s for 20 mA/cm<sup>2</sup> and 3.5 s for 30 mA/cm<sup>2</sup>). This result coincides with the theory in which pore diameters are proportional to the amount of electrolysis voltage as can be seen in Fig. 2 [18]. As the lower electrolysis voltage, the longer reaction time leads to extremely thin barrier layer due to dissolution reaction. Increasing electrolysis voltage may lead to mechanical characteristic breakdown due to faster oxidation rate, but it will increase pore diameters and decrease porosity.

#### 4. Conclusion

In this study, the following is the result of comparing oxide film generation behavior according

to the different current density using anodizing with various applied possibility and excellent physical characteristics.

1. Pore diameters and interpore distance tended to increase in proportion to the increase in the applied current density. It is determined that increased temperature by current concentration phenomenon during the reaction may have increased the activity of electrolyte.

2. Oxide film in amorphous structure was generated via anodizing, however no significant differences in pore growth behavior were observed at different current density due to low voltage and short process times.

3. Electrolysis voltage heightened with an increase of the current density, resulting in high solubility and forming larger pores in shorter time. This result estimated in which pore diameters are proportional to the magnitude of electrolysis voltage.

Different experimental conditions generate various results so that selecting the optimum condition with respect to the use and characteristics of product is the most important to apply it to the industrial field. Therefore, it is required to evaluate electrochemical and physical characteristics of anodized films based on the generating behavior of anodic oxide films.

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