Characteristics of Anodic Oxidation Process of Thin Film Aluminum deposited on Metal Substrate

Sang Hyun Seo, Yong Min Park, Young Ho Seo and Byeong Hee Kim#

Department of Mechatronics Engineering, Kangwon National University, 1 Kangwondaehak-gil, Chuncheon, Republic of Korea, 200-701
Corresponding Author / E-mail: kbh@kangwon.ac.kr, TEL: +82-33-250-6374, FAX: +82-33-259-5551

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This paper presented anodic oxidation characteristics of the thin film aluminum on metal substrate. Generally, the anodic oxidation process is performed using the high purity aluminum sheet or deposited aluminum on brittle ceramic substrates such as silicon, glass and sapphire. In order to obtain mechanical stability of substrate underlying nanoporous alumina layer, brittle ceramic substrate was replaced by metal substrates such as aluminum alloy and brass which is an alloy made of copper and zinc. In the preliminary study, surface morphologies of deposited thin film aluminum, aluminum 1145 alloy, aluminum 1050 alloy, and aluminum 6061 alloys were investigated after anodic aluminum oxidation process. Defects in nanoporous alumina were observed in Al-1145, Al-1050, and Al-6061, while No defects were found in deposited thin film aluminum. Thus, thin film aluminum was deposited on mechanical polished Al-1050 and brass for eliminating defect in nanoporous alumina. Then anodic aluminum oxidation process was carried out in oxalic acid. Surface morphologies and cross-sectional shapes of anodic nanoporous alumina on Al-1050 and brass were observed.

1. Introduction

Recently, the researchers have shown an increased interest in the functional surfaces based on nano-structures such as antireflective substrates for high-efficiency solar cells, super hydrophobic surfaces for self-cleaning materials, engineered layers for enhanced or inhibited biofilm formation, low friction surfaces for mechanical systems, and synthetic gecko adhesives.[1-5] But it is limited to fabrication of small-area substrate. For these reasons, demand for a low-cost and high throughput fabrication method for large area functional have been increased. However, conventionally reported roll-to-roll or a roll-to-flat method for fabricating large area still have disadvantages to apply to fast large-area film fabrication because their kinematic schemes are limiting a continuous process.[6-7] To overcome these disadvantages, various methods using roll-shaped mold made of laser and E-beam technique have been reported.[8-9] But, their methods are still too far from being commercialized because they use a high cost and time consuming processes.

On the other hand, during a couple of decades, the anodic aluminum oxidation (AAO) process have been drawing an attention of many nano pattern fabrication researcher because it can easily pattern a nano-hole array on the large-area surface during the low cost and short process time.[10] However, most of previous reports for the AAO processes have been remaining at the level of 2-dimensional level and even if it was formed on a roll-shaped surface that showed the material limitations in the fabrication process. Besides, defects are observed on the surface of nanoporous alumina according to the impurities in aluminum alloy. Therefore, high purity aluminum or deposited aluminum on ceramic substrate of silicon, glass and polymer by sputtering/evaporation process is generally used in anodic aluminum oxidation process to eliminate defects. Figure 1(a) and 1(b) shows the schematics of the surface of nanostructured roll mold made of aluminum alloy and that of nanostructured roll mold made of high purity aluminum, respectively. However, surface roughness of high purity aluminum is large due to its high ductility, and deposited aluminum on ceramic substrate is fragile due to brittleness of ceramic substrates. So nanoporous alumina on high purity aluminum or deposited aluminum in brittle substrate is not suitable for the mold of polymer replication process such as hot-embossing and injection molding.

In this paper, several approaches were investigated for the fabrication of nanoporous metal mold. In preliminary test, surface morphologies of deposited thin film aluminum,

aluminum 1145 alloy, aluminum 1050 alloy and aluminum 6061 alloy were investigated. Because defects were observed in all aluminum alloys, high-purity aluminum deposited on metal substrate was considered. As metal substrates, Al-1050 and brass which is an alloy made of copper and zinc were used.

2. Fabrication of nanostructures

2.1 Effect of impurities in aluminum

For the preliminary test, anodic oxidation characteristics of several aluminum alloys of Al-1145, Al-1050 and Al-6061 was compared with deposited high purity aluminum. Anodic oxidation process was carried out in oxalic acid of 0.04M during 10 min. Figure 2(a), 2(b), 2(c) and 2(d) show SEM images of surface morphologies of nanoporous alumina on deposited thin film aluminum, on aluminum 1145 alloy, on aluminum 1050 alloy, and on aluminum 6061 alloy, respectively. Aluminum composition of each film are 99.9%, 99.45%, 99.5% and 96.5%. As shown in Fig.2(a), no defects were observed in nanoporous alumina on high purity aluminum. Several point-like defects were found in nanoporous alumina formed on high aluminum composition alloys of Al-1050 and Al-1145. However, normal pore generation process was not performed in low purity aluminum alloy of Al-6061 as shown in Fig.2(d). From the results, all of aluminum alloys are not suitable to form the nanoholes without defects. Therefore, it was confirmed that the use of high-purity aluminum in order to form a uniform nanoholes.

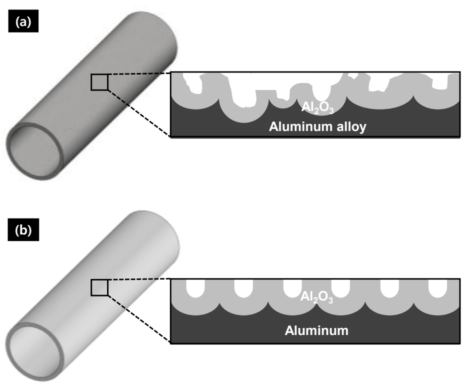

Fig. 1 Schematics of cross-section of nanoporous alumina formed on aluminum alloy (a), formed on high purity aluminum (b).

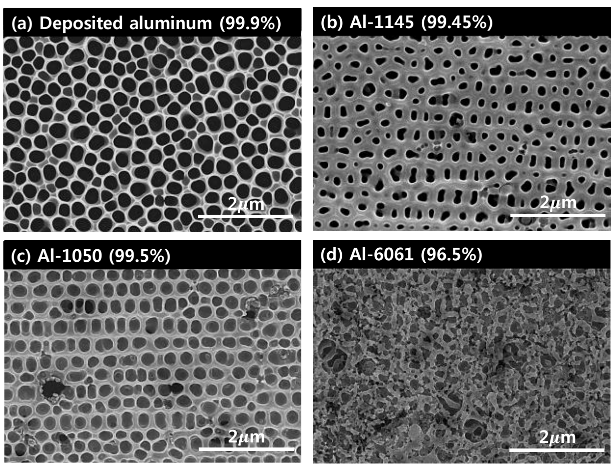

Fig. 2 SEM images of surface morphologies of nanoporous alumina on deposited aluminum (a), on aluminum 1145 alloy (b), on aluminum 1050 alloy (c), on aluminum 6061 alloy (d).

2.2 Nanoporous alumina on metal substrates

Before fabrication of the nanoporous alumina was performed, mechanical and electrical polishing processes of the aluminum alloy of Al-1050 and brass were carried out to reduce the surface roughness as shown Fig.3(a-d). In the mechanical polishing, alumina powder of 1μm was used, and electrical polishing was carried out in perchloric acid and ethyl alcohol solution ($HClO_4$+C_2H_5OH) at 20V and -5℃ for 20min.

After mechanical and electrical polishing of metal substrates, high purity thin film aluminum was deposited on metal substrates. Aluminum of 1μm was sputtered by the DC magnetron sputter equipment. Deposited aluminum was anodized in a 0.04M oxalic acid ($C_2H_2O_4$) solution at 120V and −10°C for 5min. Typically, anodic porous alumina layer which is formed in the first anodization step, and nanopore are widen to form regular nanoholes. Nanoholes of anodic porous alumina in Fig.2 were formed by nanopore widening process after the second anodization. In this experiment, however, only single step anodization was carried out to verify that the normal nanopore generation process was progressed or not.

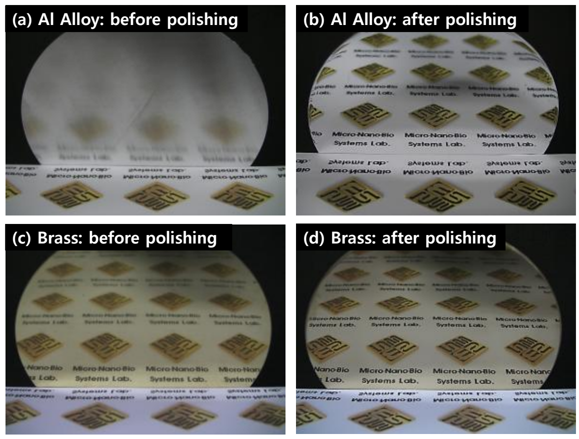

Fig. 3 Surface of metal substrate: Before (a) and after (b) polishing of aluminum 1050 alloy, before (c) and after (d) polishing of brass.

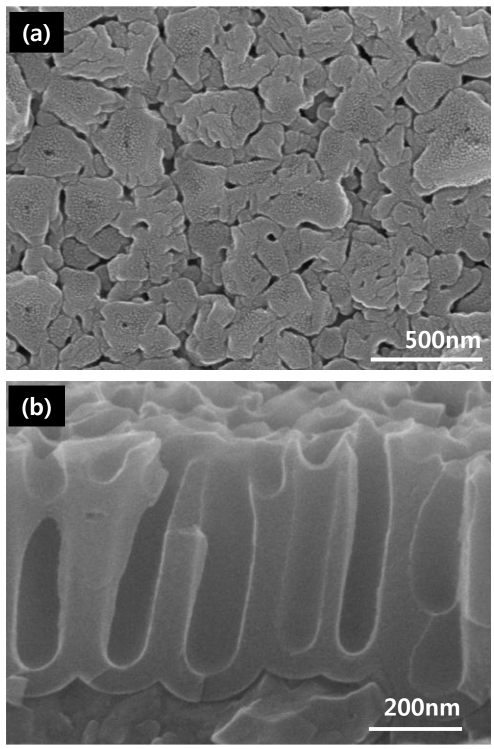

Fig. 4 SEM images of top-view (a), and cross-section view (b) of nanoporous alumina on thin film aluminum deposited on aluminum 1050 alloy.

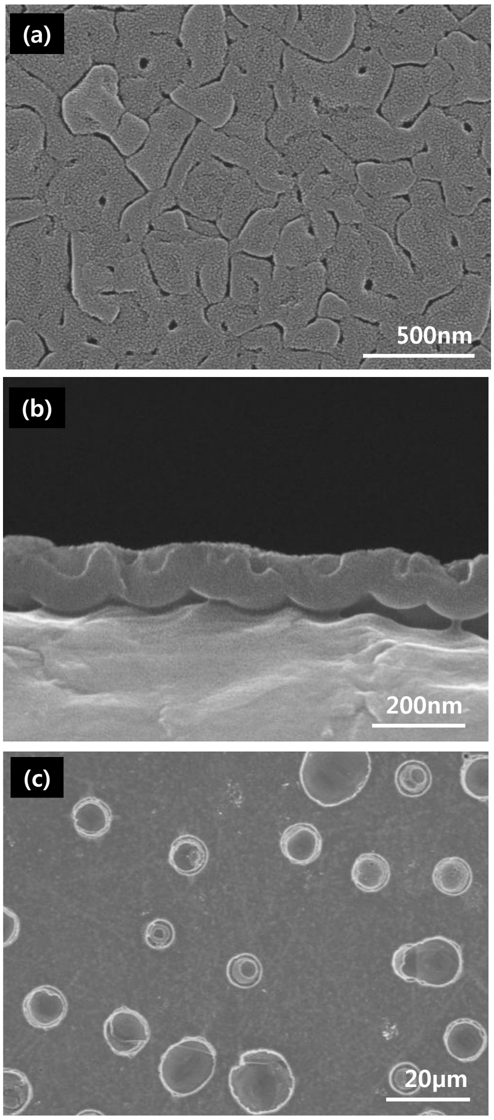

Fig. 5 SEM images of top-view (a), and cross-section view (b) of nanoporous alumina on thin film aluminum deposited on aluminum 1050 alloy.

Figure 4 shows surface morphologies of nanoporous alumina on aluminum 1050 alloy substrates after anodic aluminum oxidation. Figure 4(a) and 4(b) present top-view and cross-section view of nanoporous alumina, respectively. As shown in Fig.4, nanopores were successfully formed on thin film aluminum deposited on aluminum 1050 alloy. As the same manner, nanoporous alumina was prepared on thin film aluminum deposited on brass. Figure 5(a) and 5(b) show the top-view and cross-section view of nanoporous alumina, respectively. Nanopores were similar with those on aluminum alloys. Figure 5(c) shows the brass surface after removing nanoporous alumina and remained aluminum on brass substrate. Micropits of 5~20μm in diameter were formed on the brass surface underlying anodic porous alumina layer as shown in Fig.5(c). That means nanoporous alumina layer was floated on microcavities.

3. Conclusions

This paper presented anodic oxidation characteristics of the thin film aluminum on metal substrate. In order to obtain mechanical stability of substrate underlying nanoporous alumina layer, brittle ceramic substrate was replaced by metal substrates of aluminum 1050 alloy and brass. After anodic aluminum oxidation process, defects in nanoporous alumina were observed in Al-1145, Al-1050, and Al-6061, while No defects were found in deposited thin film aluminum. Surface morphologies and cross-sectional shapes of anodic nanoporous alumina on Al-1050 and brass were similar, but micropits of 5~20μm in diameter were formed on the brass surface underlying anodic porous alumina layer. Consequently aluminum alloy was a proper substrate candidate for anodic oxidation process of thin film aluminum.

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