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STUDY OF CRACKS IN NON-PLANAR ANODIC ALUMINUM OXIDE MEMBRANE

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ABSTRACT: *Anodic aluminum oxide (AAO) is self-assembled nanoporous ceramic structure, gaining much popularity due to its pores regularity and high surface area. During the fabrication process cracks produce at the surface of AAO non-planar membrane. This research investigates the cracks in different conditions and study the parameters involved in the generation of cracks. AAO was fabricated for different anodizing time and thickness. Cracks appeared in thick non planar membrane as compared to thin membranes. By changing the sharp edges into dull edges and reducing anodization time, cracks free transparent anodic aluminum oxide membranes were successfully fabricated. Cracks were also observed in bent aluminum sheet such as triangular and rectangular shapes. In these cases cracks were found dependent on radius to angle ratio at the edges. Various parameters such as anodization time, thickness of the membrane and cracks were studied.*

Keywords: Anodic aluminum oxide, cracks, characterization, tubular membrane, nanostructures

1. INTRODUCTION

Anodization is one of the simplest approache for fabrication of self-organized highly ordered nanostructures. In this technique an oxide layer is formed electrochemically on the aluminum (Al) surface which increases the overall thickness. This layer consists of honey comb close-packed hexagonal cells structure[1]. First planar anodic aluminum oxide membrane (alumina) was fabricated in 1984, using one step of anodization [2]. Since then it has been using for many applications such as sensors [3], filters [4], microchannels [5], photovoltaic [6], and photonics [7]. In 1996, more aligned and fine structure of alumina was introduced by Masuda et al. adopting two steps anodization [8]. This two steps mild anodization (MA) provides hexagonal structure of the pores. Several theories have been presented for the formation of self-organized structure including electric field model and mechanical stress model [9]. According to the mechanical stress model, aluminum experiences volumetric expansion during oxide formation which produces mechanical stress between the pores [10]. However it is yet to be clarified that what are the main causes of formation of hexagonal pores structure. The AAO which is ceramic and insulating materials has uniform pores perpendicular to the surface and can penetrate its entire thickness if appropriate conditions all applied [11]. Tunable pore diameters can easily be obtained from ten nanometers to hundreds of nanometers [12]. Three main techniques of anodization such as mild anodization, hard anodization and pulse anodization are adopted for the fabrication of self-organized anodic aluminum oxide nanostructure [8]. Mild anodization (MA) is slower while the hard anodization (HA) is faster process; however the drawback of the HA is the cracks on the surface of alumina. Pulse anodization which is comparatively new method that combining the properties of conventional MA and HA gives a modulated pore structure [1]. New techniques such as nanoimprinting [13], multiple beam interference lithography [14], self-assembly [15], and template-directed growth [16] are excellent contenders for the fabrication of three dimensional (3D) micro nanostructures.

Anodic aluminum oxides have also been exploiting for fabrications of 3D structures such as cylindrical, conical, triangular, rectangular, pentagonal and bowl form [17]. Three dimensional nanostructures AAO structures are more useful in modern devices. A new approach for making rectangular and tubular membrane was introduced, where cracks were utilized for cutting and shaping of the structures [18] using simple setup of two electrodes [19]. Formation of crack in the fabrication of non-planar membrane is yet a bottle neck for researchers. Still, we need more work for making crack free AAO non planar membrane. Here in this work we study the cracks in AAO structures such as triangular, rectangular and small angle shaped structures. We described the methods to control or minimize these cracks for three dimensional AAO structures. In this research we successfully fabricated cracks free non planar membranes.

2. EXPERIMENTAL DETAILES

A. Anodization of solid Aluminum:

To observe the cracks at the edges of rectangular structures, 1mm thick Al sheet was cut from 99.56% pure Al, special care was taken to make uniform and symmetrical rectangular piece of Al from large sheet. For precise cutting, electric discharge machining (EDM) technique was used to avoid any bending at the edges of these small 3D structures. Prior to anodization, aluminum sheet was annealed at 450oC in the presence of nitrogen gas in order to remove the mechanical stress occur in the sample after cutting. Subsequently Al samples were cleaned and rinsed in de-ionized (DI) water for 10min. The electropolishing and anodization was performed in two electrodes experimental setup. Briefly the setup consists of strong cooling system and magnetic stirrer for maintaining low temperature and uniform chemical concentration. Electropolishing was conducted at 18 volt in the mixture of perchloric acid ($HClO_4$) and ethanol (C_2H_5OH) for 3-12 min. For observing the cracking effect electropolishing were done for two different timing. After 3 min electropolishing the edges remained sharp while after 12 min electropolishing the edges turned round (dull). For removing the electropolishing solution, ultrasonic cleaning was done in acetone and DI water. Two steps of anodization were performed for getting uniform pore and hexagonal structure which give strength to structure. In the two steps anodization first step was conducted for few hours in 0.3M oxalic acid under the applied voltage of 40V. During AAO growth temperature was kept zero degree Celsius. After te first step of anodization irregular growth was removed in phosphoric and chromic acid at 80^{o}C for 8-12 min depend upon the growth thickness. The second step of anodization was carried out for longer time (6 - 48 h) under same conditions.

Aluminum samples of different thickness from 0.2 mm to 1 mm were anodized to observe the cracks in the structure. Initially anodization of 1 mm thickness sample was conducted for 24h, prominent cracks appeared at the edges as shown in Fig. 1 (a and B). When the sharpness of the edge was reduced crack free structure was obtained as shown in Fig.1(c).

B. Fabrication of L-shaped and Triangular structure:

For triangular and perpendicular bent structure, aluminum of 0.2 mm thickness was annealed, electropolished and anodized adopting the above mentioned procedure. Plane aluminum sheet were bent for making triangular and L-shaped structures. The edges of structures were made dull in order to get high radius to angle ratio at the corners. Subsequently electropolishing and two steps anodization were carried out as explained above.

3. RESULTS AND DISCUSSION

In this research, we overcome the cracking effect during the anodization. Three dimensional crack free structures were fabricated such as L-shape, rectangular and triangular.

A. Cracks in AAO using Al block:

AAO were fabricated on rectangular aluminum blocks. After 24 h of anodization the AAO experienced cracks prominently at every edge less electropolished (4min) sample having sharp edges while no any crack appeared in the other sample which was electropolished for double time (8min) as shown in Fig. 1. For characterization of cracks the anodization time was varied from 2 h to 36 h using same dimensions of rectangular Al sample. Up to 8 h of anodization, no crack appeared at any edge but when anodization time was increased from 9 h, cracks appeared in one sample.

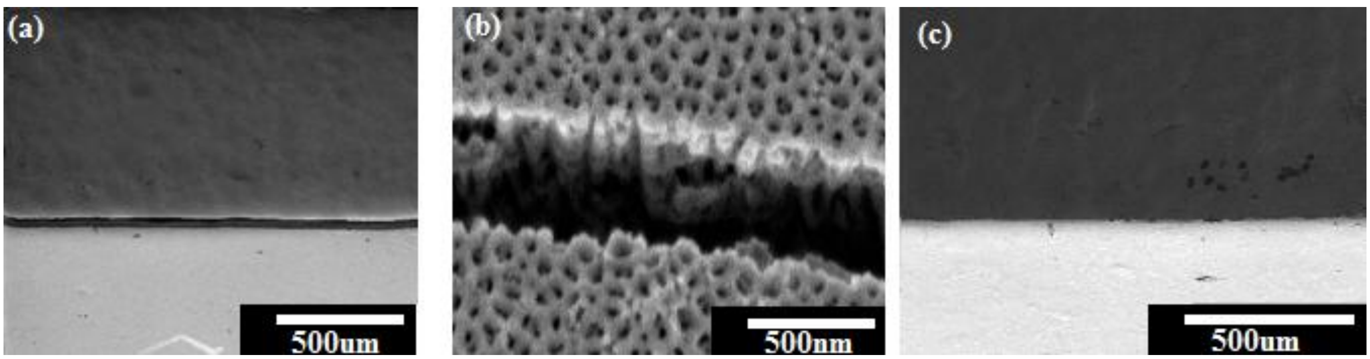

Fig (1) FE-SEM images of solid alumina edges: (a) Formation of crack at 3D sharp angle (b) magnified image showing the crack (c) 3D crack free dull angle edge having high radius of curvature.

We preceded our experiments by increasing the anodization time. As explained in the methodology the edge sharpness of Al samples was reduced by varying electropolishing time. After 3 min of earlier electropolishing Al edges were remained sharp but after 12 min of electropolishing the edges of rectangular shaped Al turned rounded in shape. The anodization was continued till 36 h. The cracks appeared in all sharp edges after 8 h of anodization of the sample. After 12 h of anodization, one sample suffered from wide and prominently cracks while the other having rounded edges remained crack free. Figure 1 (a and b) elaborate the FE-SEM images, cracking effect occur at sharp edges and dull edges of the rectangular solid piece of samples remained safe.

These results show that cracks appeared in one of the solid block while the other sample is crack free having same dimensions. The reason is the sharpness at one sample where proper place was not available for growth on the surface and when the mechanical stresses increase the specific value then this stress need to release so creak generate at the edges of the fragile ceramic structure. Here it is worth mentioning that the corners are integral part of some circle, if the circle (curvature) is small it means radius to angle value is high as compare to large circle where radius to angle ratio is low so cracks will not generate. Figure 2 elaborates the radius to angle ratio in both cases, where the arc is the integral part of a circle and ‘r’ is the radius.

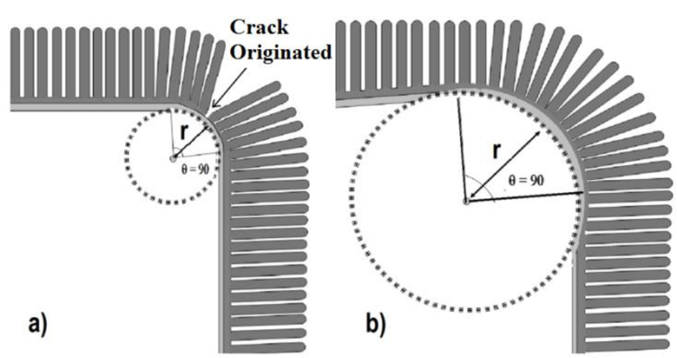

Fig (2) Schematic of the anodization at bends, (a) crack formation at sharp angle having very small radius, (b) no any crack appeared in the structure due to large value of radius to angle ratio

Fig (3) Optical and SEM images of the AAO grown structures (a) triangular structures which clearly show the expansion of angle from 60^o to 73^o ultimately released mechanical stress, avoiding cracks as shown in Frg.4 (b) in the Fig.4 (c) uniform diameter nanochannel perpendicular to the surface.

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B. Triangular and L shaped structure:

AAO was also fabricated from Al sheet bending into different shapes such as triangular and rectangular without connecting two ends. It was observed that these structures widened the gap after anodization (in triangular case), which automatically released stress evaded the cracks. After 32 h anodization, triangular shaped Al expended its angles from 60^o to 73^o producing gap as shown in Fig. 3(a). Similarly Fig. 3(b) shows, L-shaped Al extended angle from 90^o to 96^o. In both cases AAO membrane was found crack free. When AAO was fabricated with sufficient thickness (for more than 48 h), it produced cracks. The formation of these cracks initially originates from surface and then move towards volume expansion. This volume expansion generates tensile stress at the Al/Al_2O_3 interface, this stress has to be released otherwise reaches to a critical value where radial cracks generate. It is important to mention that crack gives relaxation in stress in near area which decreases the tensile stress. The larger bend can reduce the crack due to sufficient space or planar behavior at arc having The FE-SEM images of the AAO structures are shown in Fig. 4, in which different sides has been shown. It is worth mentioning that AAO has very fine, uniform pore hexagonal structure in the planar surfaces as compare to edges because mechanical stress applied during the bending, disturb the internal grain structure consequently irregular pore structure grows as shown in Fig. 1(b). Figure 4 (a) shows the uniform hexagonal pore planar surface structure, Fig. 4 (b) shows barrier layer while Fig. 4 (c) shows the nanochannel cross section image. The average pore size is 50-60 nm.

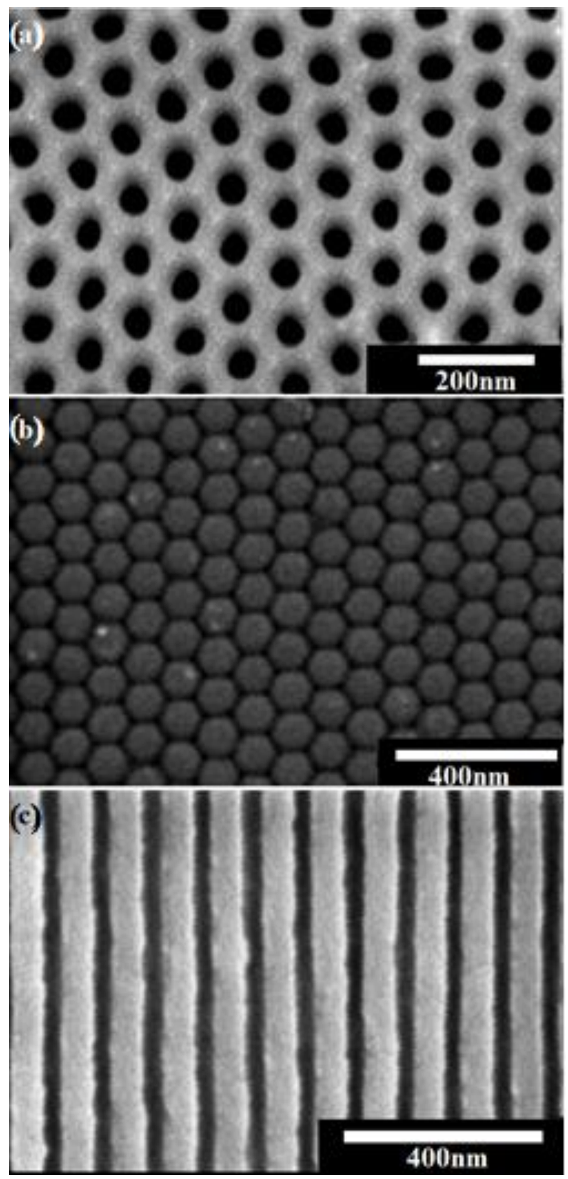

Fig (4) SEM images of self-organized AAO structures (a) uniform hexagonal pore planar surface structure, Fig. 4 (b) shows barrier layer (c) nanochannel cross section image

4. CONCLUSIONS

In this research, three dimensional AAO structures were fabricated under various conditions to avoid cracks in the structures. The parameter which causes the crack generation were studied and characterized. The main finding was the abrupt and sharp bend in the structure which causes the cracks. In this work L-shape, rectangular and triangular structures were fabricated successfully without crack. In all the mentioned structures avoid the sharp edges by reducing the radius to angle ratio at the curve. In the future work we will extend our research involving other electrolytes such as sulfuric, phosphoric and malonic acids. Besides the used parameters other important parameter 'growth rate' which may provide more opportunities to researcher in the field for selecting correct anodizing conditions.

5. REFERANCE

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