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A Review on Studies of Mechanical Properties of Anodized Alumina Oxide

Rajesh Beri [1], Manoj Kumar Kushwaha [2], Neelkanth Grover [3]

[1] Research Scholar, I. K. Gujral Punjab Technical University, Kapurthala-144603, Punjab, India
[2] Department of Mechanical Engineering, Shaheed Bhagat Singh State Technical Campus, Ferozepur-152001, Punjab, India
[3] Department of Mechanical Engineering, I. K. Gujral Punjab Technical University, Kapurthala-144603, Punjab, India

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Abstract - *This review paper is an overview of the current state of research on AAO (anodized alumina oxide). Due to applications in electronics, optoelectronics, energy storage, photo catalysis, photonics and biosensors/biomaterials, interest in one dimensional nanostructures has grown significantly during the last decade. Anodization is done on alumina electrochemically resulting in to formation of anodic oxide layer. Nanostructures thus formed are an array of closely packed hexagonal oxide cells, in the centre of each of which there is a vertical hollow channel. These honeycomb shaped structures thus formed have been well exploited in traditional engineering applications for their unique mechanical properties including large strength-to-weight ratio, high anisotropy, extended plastic plateau corresponding to strain localization, and so on. Mechanical properties like young's modulus, hardness, and fracture toughness of the Nano porous alumina are measured by Nano indentation. This method makes use of very low loads in the milli newton range for application on AA0. Studies show that the pores greatly improve toughness of the porous alumina. When the pore diameters of AAO structures are investigated using Nano indentation, the smallest pore diameter produces the highest hardness value. The analysis of the hardness–contact depth data reveals that the indentation hardness decreases in inverse proportion to the indenter penetration depth. Furthermore, the corresponding hardness remains constant despite the increase in indenter depth. When the specimen is subjected to heat treatment at 650°C, it causes the hardness to increase from 5.2 to 6.36 GPa and the fracture toughness sharply decreases. The study of the structural and magnetic properties of ferromagnetic nanotubes in aluminium oxide templates with different diameters, wall thicknesses, and lengths shows that magnetization processes of nanotubes is influenced by the wall thickness. In wear study, in sliding contact situations, aluminum has poor wear resistance and high friction. The naturally occurring oxide layer that forms will protect the base substrate from corrosion but is not effective for wear resistance due to inadequate thickness in its natural state. The sulfuric anodizing process found to be an economical and effective way to improve the wear characteristics of this oxide layer. Hard anodizing, at lower electrolyte temperatures, allows for thicker, denser build up of the oxide due to smaller pore size. This greater dense formation of the nanotubes with small pore diameter results in higher micro hardness of the oxide layer as compared to the base substrate. Hard anodizing is an effective method to improve the friction and wear characteristics of aluminum by increasing the thickness of oxide formation on alumina surface.*

Key Words: **Anodization, nonporous, Nano-indentation, young's modulus, toughness.**

1. INTRODUCTION

The anodization process has been used by industry to protect metal components from corrosion for approximately 90 years. By using an electro-chemical process the surface chemistry of the metal is changed, via oxidation, to produce an anodic oxide layer that is thick enough to stifle further oxidation. Aluminum metal (Al), because of its high strength to weight ratio, numerous engineering applications [1, 2] is a widely used metal and is also easily available. For nanostructures Al is generally used in form of AAO. Two types of anodic Al oxide exist; the first is a non-porous barrier layer that is thin, hard, and wear resistant and behaves as an electrical insulator. The second, a thicker porous oxide structure, is called AAO layer [1]. This layer structure has a high aspect ratio and consists of a porous structure. The structure of AAO, is very stable at high temperature and in organic solvents, and exhibits uniform pore density, and the pores are parallel and perpendicular to the surface, having an ideal cylindrical shape. Thus anodization is increasingly becoming the subject of many investigations in several fields. The most recent advancement in application of AAO is the fabrication of capacitive humidity sensors because the nano sized pores provides a large surface area for absorbing water vapor. A thick porous layer i.e. structure having large pore diameter results an increase in sensitivity because of an increase in contact surface area [8]. Furthermore, the porous AAO membrane itself is employed for filtration, gas separation or as photonic crystals [3].AAO membrane itself is employed for filtration, gas separation or as photonic crystals [3].

1.1 ALUMINUM OXIDE, [AL_2O_3]

Anodizing is a process that results due to the natural tendency of metals to oxidize under atmospheric conditions. Al is a reactive metal that reacts readily with the oxygen present in the atmosphere at ambient temperatures to create a thin amorphous oxide layer (1- 10 nm thick). The thickness of this oxide layer is temperature dependent and at temperatures above 500 °C, both amorphous and crystalline alumina are present [3]. This layer has the advantage of preventing further dissolution of the Al and thus provides an effective protective barrier. During the anodization process, Al produces a highly impervious protective layer on its surface. The anodic layer parameters such as barrier layer thickness, pore diameter and pore height are directly dependent upon the voltage used in the anodization process [5-7]. The occurrences of various changes on Al specimen with various ranges of voltage and current are shown in figure 1, which represents that at low voltages and high currents, pitting at the crystallographic boundaries begins, while at higher voltages and lower currents, electro-polishing effects take place. As the voltage is further increased, the current decreases and a porous layer will form. And finally, at extremely low currents and high voltages, a thick layer of Al oxide is formed. Temperature, electrolytic solution and electric current are the major process variables in this process. By varying these variables desired output can be obtained (in the form of pore size, pore diameter, pattern of pore formation etc.). In anodization Al work piece is attached to the positive side of a DC power supply and placing it into the suitable electrolyte called bath. Another electrically conductive metal, inert in the anodizing bath, is connected to the negative side of the power supply.

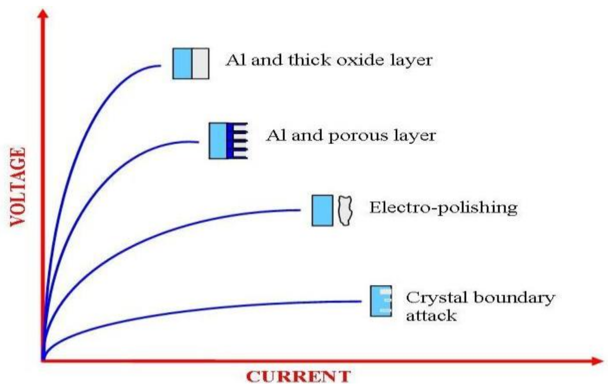

Fig- 1: Occurrences of changes on an Al. sample; represented on voltage vs. current plot [1]

On activating the power supply, electrons are pulled from the Al into the solution causing the Al to react with water to form an oxide layer. At the cathode, hydrogen gas is formed.

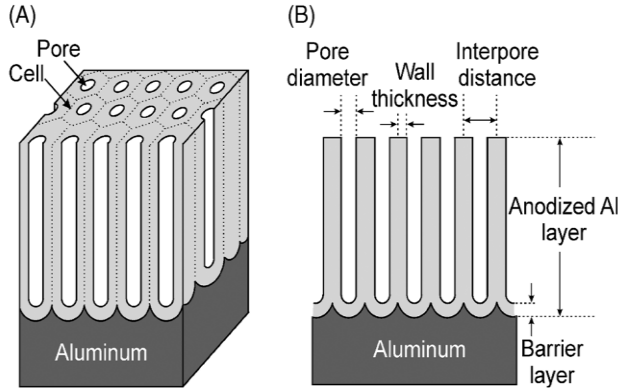

Fig - 2: Idealized structure of anodic porous alumina (A) and a cross-sectional view of the anodized layer (B). [3]

As the oxide layer develops, the sulfuric acid in solution continues to partially dissolve the aluminum substrate and oxide layer. This is replaced by the volume of oxide growing on the surface in the form of hexagonal cells with hollow cores as shown above in the figure showing the idealized structure of anodic porous alumina and the cross-sectional view of the anodized layer.

In 1970, O'Sullivan and Wood presented a model to describe self-regulating pore growth. During the anodization process with in an acidic medium, the Al surface is oxidized where the oxide layer consists of a self organized nano-porous structure. Masuda and Fukuda recently focused on AAO nanostructure & its fabrication using the two-step anodization process. Two-step anodization process is proved to be very vital in regulating the nano-porous structure, since irregular nano-pores are formed on the Al substrate after the first anodization [3]. But two-step anodization generates an ordered pore array throughout the entire oxide layer. Well-ordered nanopore arrays are obtained by etching out the oxide layer with irregularly arranged nano pores towards the film surface. So by using this two-step method, Masuda and Fukuda obtained a well ordered and hexagonal nanopore array [3]. As proposed by Masuda and Fukuda, AAO templates are produced by two step anodization by firstly pre-cleaning the Al substrates. Then after pre-cleaning first step of anodization is done on Al by applying an appropriate potential and Pb. is used as cathode in an acidic electrolyte, although several acids can be used and are essential for fabricating different pore sizes, but sulphuric acid is the most commonly used electrolyte. With sulphuric acid (H_2SO_4), templates with maximum pore diameter about 40 nm can be obtained. The process usually is carried out in 0.3M H_2SO_4 at 5ºC and by applying 40V anodization potential. After first step the Al substrate is ready for a second anodization. This step is similar in terms of anodization conditions such as the applied potential, temperature and concentration of acid but different in duration of the anodization. The duration of the first anodization is generally about 1 hour whereas that of the second anodization varies from 2 to 7 hours depending on the desired pore size and the pores obtained are very uniform after second step anodization. However Kirchner and co-workers fabricated AAO membranes by one-step anodization process. They used, Al electrodes (25 mm × 10 mm), and then these are degreased in acetone and cured for 2 hours at 80ºC. The specimens were anodized in 0.3M H_2SO_4 electrolyte for about 12 hours at a constant potential of 25.0V with a platinum cathode, at 7ºC. The pores on the metal were opened by etching in 5% H_3PO_4 for 60 minutes at 30ºC. A three step anodization has also been used as a method to fabricate self-organized nanopores in oxalic and sulphuric acid [1] by using the three different time intervals for three different steps. For example, Feiyue Li *et al.* used 5–10 minutes, 0.5–12 hours and 3 minutes for the three respective steps in their anodization of Al. It was found that the order of self-assembled nanopore structures is comparable between the three-step anodization, and the two-step anodization processes. Brandli *et al.* used 0.3 wt% oxalic acid electrolyte for anodizing Al and a wet chemical etching solution, comprising 1:1 chromic acid (0.4%) and phosphoric acid (0.6%), for selective Al oxide stripping[3]. The electrode was immersed in this solution for 6 min at 60°C for each etching step. The results prove that by increasing the number of anodization-etching, an increase in the uniformity of the pore size and the pore diameter can be achieved.

2. MECHANICAL PROPERTIES OF AAO

Alcala et al. conducted a detailed study of the mechanical properties of porous anodic alumina (PAA). Literature shows that very less research has been conducted on the mechanical properties of PAA films. Alcala *et al.* [2] measured Young's modulus and hardness of highly ordered nano porous alumina by nano-indentation. Nano-indentation makes use of depth sensing indentation tests, in which an indenter is pressed into the surface of a test specimen and both the indenter load P and the indenter displacement h into the material are continuously recorded during the entire test. This provides a load displacement curve $(P–h)$, which is a "fingerprint" of the mechanical properties of the tested material, from which the hardness and elastic modulus can be calculated [3]. The fracture mechanisms of the materials and effects of heat treatment on the mechanical properties of the materials were also investigated. Numerical models were developed to calculate Young's modulus and hardness of the PAA. The results show that the heat treatment does not change the Young's modulus but strongly affect the fracture toughness of the alumina.

Z. Xia et al. conducted experiments by subjecting their specimens to nano-indentation, using a Nano indenter® Model II with a Berkovitch indenter and a cube-cornered indenter, on the top and side of the porous alumina [6]. The Berkovitch indenter was used primarily to measure hardness and elastic modulus. Loads of 20-650 mN were used for cube-cornered indentation. The results elicits that the average value of young's modulus E for the alumina is approximately 140 GPa, with a small variation of less than 10% of the value. The heat treatment does not affect Young's modulus but it does increase the hardness of the porous alumina. After heat treatment, the hardness increases by 20%.

Mahdavian & Mai studied the wear properties and noted that Al. is very poor in wear properties because the Al. debris generated in the sliding process were initially small but became larger in size with increasing sliding distance and can cause severe damages on the sliding surfaces of the specimen and also results in transfer of aluminum wear particles in large lumps due to adhesive forces acting between the particles. Another study discusses a process of wear called galling in which there is formation of surface protrusions when two solid surfaces experience relative sliding under load. Very limited research has been done on the effect of hard anodizing on wear resistance. Since aluminum is a soft metal that does not withstand well in wear situations, the development and understanding of ways to improve the wear characteristics and durability of this protective oxide layer is critical [7]. Generally, it is understood that abrasive wear resistance increases with hardness, but this is not always true [8]. Scratch tests of hard anodized (thickness of about 20 μm) versus bare aluminum indicated the thicker oxide treatment "induces the transition of wear mechanism from ductile to brittle damage". In the end, this test shows that increasing hardness by hard anodizing aluminum decreases abrasive wear resistance [11].

Recently, magnetic nanowire arrays have been attracting much interest owing to their potential applications for high-density magnetic memories, single-electron devices, optical media, photonic- band-gap materials and high-sensitivity giant magneto-resistance (GMR) sensor [12]. AAO pores are best suited as template compared with other templates, because the pore size of AAO can be readily controlled by anodizing. The pore diameter, the inter-pore distance (cell size) and the barrier layer thickness are controlled by using the anodizing voltage, and the depth of the pores is controlled by using the anodizing time [6]. To fabricate an adaptable AAO template, we used a modified two-step anodization method. The general procedure for the fabrication of nanowire arrays is an electro deposition method. The electro deposition method is a low-cost, high-yield technique for the fabrication of nanowires in an AAO template [12]. CoNiP NW (nano wires) arrays were synthesized by electro-deposition inside the nano channels of AAO templates, and the corresponding structure and magnetic properties were characterized. The results indicate that the magnetic properties strongly depend on the component contents and crystal structures of CoNiP NWs, the synthesized CoNiP NWs are polycrystalline embedded with Co and Ni nano-crystallites and have hard magnetism with large magnetic anisotropy. On the other hand, under room temperature, the synthesized NWs are monocrystalline. The porous AAO was fabricated using a two-step anodization process. The studies of the magnetic properties of the Ni nanowires and the post-annealed Ni nanowires (at 600 °C in air) show that the annealed Ni nanowires have smaller ferromagnetic saturation than the un annealed Ni nanowires. This result indicates that NiO existed in the Ni nanowires after the post-annealing process. In addition, the magnetic properties of the Ni nanowires at 5 Kelvin showed that the easy magnetization axis in the annealed Ni nanowires had rotated from the parallel to the nanowire surface to the perpendicular to that surface. Since the shape anisotropy of continuous Ni thin films favors the direction of the easy magnetization axis being parallel to direction of their surfaces, these results show that at low temperatures, the magnetic properties of Ni nanowires behave as those of continuous Ni thin films [12].

3. CONCLUSIONS

Two-step electrochemical anodization results in well-defined, self-ordered, porous alumina structures of Al electrodes in several electrolytes. Both anodization time and applied potential affect the regularity and size of the nano pores, although the effect of the potential appears to be stronger than the effect of temperature in the transformation from crystalline alumina to amorphous alumina. While the inter-pore distance is linearly proportional to the applied potential, pore diameter remained independent of the acid concentration [3]. But in sliding contact situations, aluminum has poor wear resistance and high friction, especially in aluminum on aluminum scenario. The naturally occurring oxide layer that forms will protect the base substrate from corrosion but is not effective for wear resistance due to inadequate thickness in its natural state. The sulfuric anodizing process is an economical and effective way to improve the wear characteristics of this oxide layer. Hard anodizing, at lower electrolyte temperatures, allows for thicker, denser build up of the oxide due to smaller pore size. This greater density results in higher micro-hardness of the oxide layer as compared to the base substrate. Brittle fracture of the oxide replaces ductile failure at the surface creating debris that contributes to third body wear at a lower rate. Hard anodizing is an effective method to improve the friction and wear characteristics of aluminum in many applications [3]. Young's modulus, hardness and fracture toughness of highly ordered nano porous alumina (PAA) were measured by nano-indentation. The principal results are:

- Accounting for pores, Young's modulus of the alumina is determined as 140 GPa. Heat treatment at 650 °C does not affect the Young's modulus.
- After annealing hardness of the alumina increases from 5.2 to 6.3 GPa while the fracture toughness decreases.

Where the mechanical properties of AAO structures are investigated using nano-indentation, the smallest pore diameter produces the highest hardness value. The analysis of the hardness–contact depth data reveals that the indentation hardness decreases in inverse proportion to the indenter penetration depth. Furthermore, the corresponding hardness remains constant despite the increase in indenter depth.

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BIOGRAPY

Rajesh Beri (First Author) is a Research Scholar of I. K. Gujral Punjab Technical University, Kapurthala.