

FORMATION OF ANODIC POROUS ALUMINA IN OXALIC ACID AND ELECTRODEPOSITION OF NI.**Khamidov Anvar***Doctorate of 2-course of the National University of Uzbekistan***Nurmanov Suvankul Erhanovich***Doctor of technical sciences, professor,**Faculty of chemistry of the National University of Uzbekistan***Ruzimuradov Olim Norbekovich***Doctor of chemical sciences, professor,**Faculty of chemistry of the National University of Uzbekistan***Parmonov Askar Basimovich***Doctor of philosophy sciences (PhD), Faculty of Chemistry of National University of Uzbekistan*DOI: 10.31618/nas.2413-5291.2020.2.60.303**ABSTRACT**

Nanoporous anodic aluminum oxide (AAO) tubular membranes were fabricated from aluminum alloy tubes in sulfuric and oxalic acid electrolytes using a two-step anodization process. The membranes were investigated for characteristics such as pore size, interpore distance and thickness by varying applied voltage and electrolyte concentration. Morphology of the membranes was examined using light optical and scanning electron microscopy and characterized using Image software. Results showed that membranes having narrow pore size and uniform pore distribution with parallel channel arrays were obtained. The pore sizes were ranging from 10 to 100 nm and the wall thicknesses 60 μm .

The catalysts are obtained by impregnation of 3d metals into nanosized pores of aluminum oxide. The obtained catalysts based on nickel and porous Al_2O_3 are studied by scanning microscopy (SEM-EDX). The results of SEM-EDX analysis shows that a spongy structure with filament sizes of 100 nanometers containing particles of 3d metals formed on the surface of the aluminum oxide matrix.

Keywords. Nanoporous anodic aluminum oxide (AAO), carbon nanotube (CNT), tubular membrane, thickness, anodising, porous aluminium oxide film.

1. Introduction

Electrochemical oxidation, also known as anodizing, imparts an integral corrosion and abrasion resistant coating on industrially important metals. Aluminum and aluminum alloys have been treated using anodizing for nearly a century. These metals react spontaneously with ambient oxygen to form a thin oxide coating. Unlike other metal oxides, aluminum oxide does not flake; the oxide adheres to the metal preventing further oxidation. To exploit the corrosion and abrasion protection provided by aluminum oxide, forced thickening of the coating is accomplished electrochemically.

Anodization is an electrochemical oxidation process employed to increase the thickness of the native oxide layer on the surface of metals (e.g., Al, Ti, Hf, W, Nb, Sn, Zr, etc.) or semiconductors (e.g., Si, InP, GaAs, etc.) [1].

Nanoporous anodic aluminum oxide (AAO) has become a commonly used material with potential applications in a wide range of areas, such as catalysis, electronics, photonics, and sensing. Owing to their regular structures and narrow size distributions of pore diameters and interpore spacings, porous alumina membranes are used in the fabrication of nanometer-scale composites. The nanoporous AAO sheet membrane has been investigated for a potential application in hemodialysis by measuring the hydraulic conductivity and comparing it to those of hollow fiber polymer dialysis membranes. It is known that carefully controlled anodization of aluminum in an acidic electrolyte produces a thin layer of dense aluminum

oxide, followed by an ordered array of smaller-sized nanopores [2,3].

The main disadvantage of the catalysts based on nickel nanoparticles is the rapid deactivation of the catalyst due to various factors, for example, coke deposits. To prevent agglomeration and sintering, the active phase is applied to various inorganic substrates — Al_2O_3 , SiO_2 , and CaCO_3 [4]. The use of films, for example, Al_2O_3 as a matrix, allows combining the flexibility of the electrochemical method for obtaining catalysts and stabilizing nanoparticles in the inert matrix of porous aluminum oxide. Catalysts on substrates have several advantages, but they have low thermal conductivity. In this regard, it is relevant to create and study of nickel catalysts on metal substrates, to identify patterns of influence of synthesis conditions on the surface structure and to establish the relationship among synthesis conditions, surface structure, and such catalytic properties as an activity, stability of activity and resistance to carbonization of catalysts in the hydrogenation of olefins. Also, it is very important to have a developed surface for all metal catalysts, i.e. search the ways to increase their specific surface area.

Indeed, the establishment of their structure and nature of interaction with reagent molecules provides valuable information on the mechanisms of catalytic processes. It is the substrate that largely determines the size, shape, and the electronic state of the deposited particle [5-7].

Anodic aluminum oxide ~ AAO, which is usually prepared by the anodic oxidation of Al in an acid solution [usually sulfuric (H_2SO_4), oxalic ($\text{H}_2\text{C}_2\text{O}_4$), or

phosphoric (H_3PO_4) acids] [6], is one of the typical self-organized structures with a nanochannel array. Thus AAO has been commonly used to fabricate nanometer-sized structures via the template-mediated process because of its relatively low cost and ease of fabrication compared with conventional lithography-processed materials [8].

Recently, many researches have been focused on the nanostructured materials due to some of their significant physical properties. Although several techniques like photolithography, etching, or gas phase synthesis can produce nanowires or nanotubes, a template-assisted growing approach of nanoporous AAO is considered as one of the most prominent methods due to the advantages of a controllable diameter, high aspect ratio, and economical way in producing [9].

In this study, acid solution was used to create the aluminium oxide film with controlled morphology. However, the porous aluminium oxide film properties is strictly influenced by anodising process parameter such as anodising voltage, electrolyte temperature, acid

concentration and duration of anodising process. Thus, in this study new hypothesis will be generated with exploring the relationship between electrolyte temperature and formation of aluminium oxide film on aluminium substrate in order to enlarge its applications.

2. Experimental part

In our experiment a high purity aluminum foil (99.999% purity, 5 mm thickness) was used as a starting material. Prior to anodizing the aluminum foil was annealed at 500 °C in air for 2 h and degreased in acetone. Then the samples were electropolished at room temperature in 1:4 volume mixture of $HClO_4$ and ethanol at constant current density at 25 mA/cm² for 5 min. The hard anodization technique was applied using oxalic acid containing 0.1 M as electrolyte. During the anodization the electrolyte temperature of all samples was kept constant at 20-25 °C. This anodising process was done at 40 V with temperature for 120 minutes.

Anodizing of Al-plates is carried out in a two-electrode chemical cell which is a Teflon glass with 4 sm opening in diameter in this area and mounted on a brass stand (Fig. 1).

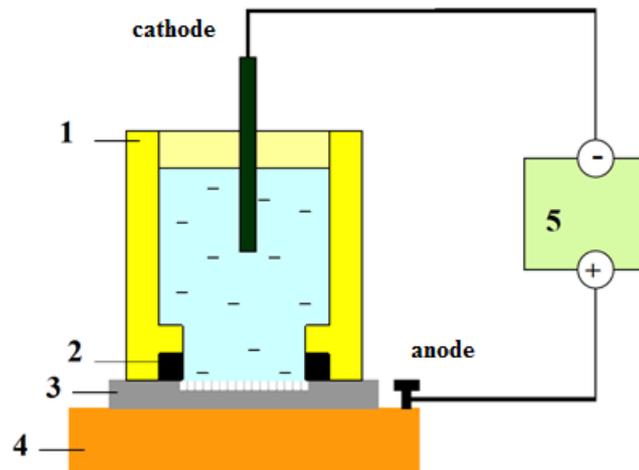


Figure 1. Experimental equipment used to produce anodized aluminum oxide. 1-Teflon glass, 2-rubber seal, 3-sample (Al-foil), 4-brass base, 5-voltage source.

The conditions of anodic oxidation depending on the selected electrolyte is given in Table 1.

Table 1.

The conditions of anodic oxidation

Oxidation steps	Electrolyte	Anodizing voltage and current, B; A	The duration of oxidation, hours
The first oxidation	0,1M (COOH) ₂	40; 2	1
The second oxidation	0,1M (COOH) ₂	40; 2	1

The preanodization step for 10 min was applied to produce a thin porous oxide layer (about 500 nm thick) to create a protective layer against burning at high voltages [10]. As we know in each electrolyte mixture [11] the appropriate voltage for pre-anodization is related to the current and we choose this voltage such that the current density to be in the range of 1.5 mA/cm² < J < 2.5 mA/cm². After preanodization (in voltage lower than 40 V), the anodization voltage was increased to a final constant value by a suitable rate that is exactly

related to the concentration of sulfuric acid [11]. To investigate themorphology and self ordering degree of nanopores, the SEM images were taken from the Al surface (imprint barrier layer) after selective etching of the porous alumina film by a mixture of 6 wt.% H_3PO_4 and 1.8% H_2SO_4 at the end of each process. The morphology and structure of porous aluminium oxide film obtained were characterised by Scanning electron microscope (SEM) model NVision 40-38-50 SEM.

3. Electrodeposition

Metal/metal alloy can also be filled into the nanochannels of AAO-CNTs using a conventional electrodeposition technique. When an electric field is applied, metal ions in the electrolyte solution migrate and are deposited onto an electrode by passing a current through an electrochemical cell. Therefore, metals can be filled into the cavity of AAOCNTs by using the electrodeposition method under a direct current [15-17] or alternating current [18]. In general, a layer of Au is first deposited on the surface of a both-side open AAO film using ion sputtering technique. Then, metal foreigner can be deposited into the hollow core of AAOCNTs by using the pre-deposited Au layer and

graphite plate as working-electrode and counter-electrode, respectively. However, it is rather difficult to handle during the electrodeposition process owing to the fragile property of AAO films.

The synthesis of nickel nanoparticles into a matrix is carried out by the method of periodic dipping with sequential drying. The aluminum oxide porous plate is alternately dipped in aqueous solutions of $\text{Ni}(\text{NO}_3)_2$, then it is washed in water, dried and again immersed in the solution. After a certain number of impregnation cycles, the plate is annealed in the air at 550°C .

Basic geometric parameters of experimental samples and parameters of the surface morphology of Ni columns for samples. (Table 2.)

Table 2.

Properties	Diameter pore, nm	Interpore diameter, nm	Cross-section pore, μm
AAO	90 ± 25	90 ± 25	80 ± 20

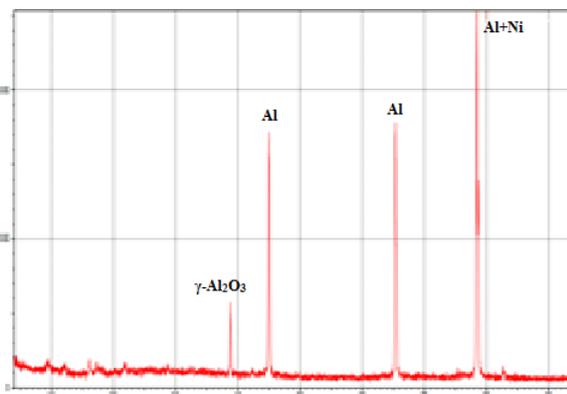
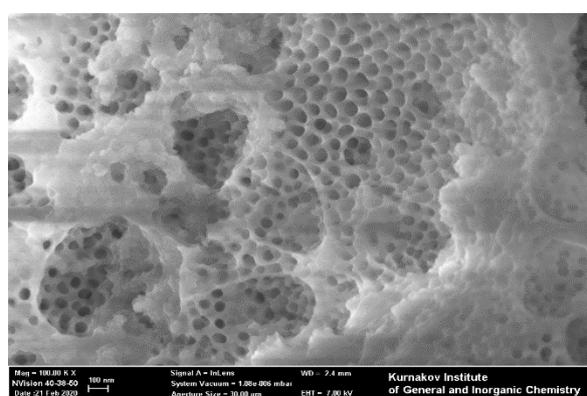


Figure 2. XRD analysis diffraction of aluminium substrate.

4. Results and discussion

The advantage of using porous alumina as a template is that it enables selected nano-pore fabrication using general laboratory equipment, see Figure 1. The proportionality of the cell size with respect to the electrochemical conditions allows one to macroscopically dictate the growth and final size of the pores manufactured. The equation is a simple one where an Al substrate is used with a particular acid to achieve nano-pores with an empirical derived set of electrochemical conditions.

$$\text{Al} + \text{acid} + \text{voltage} = \text{nano-pores}$$

Initially, the quality of the Al substrate, its surface structure and/or any surface pre-treatments will have a significant impact on the morphology and the resulting nano-structures formed on the substrate surface during the anodization process. To begin with, the Al substrate will have a pre-existing oxide layer over its surface,

which is normally produced by the ambient oxygen in the atmosphere. In addition, the substrate could also have a pre-existing surface structure produced by a mechanical, thermal, chemical and electrochemical process. All of these surface treatments prior to anodization can have a significant impact on the self-ordering of the pore structures that form on the surface of the substrate during the anodization process. This is because the pore nucleation mechanism is a combination of both random nucleation and nucleation produced by the effects of surface defects, such as scratches, pits, impurities and grain boundaries. It should also be pointed out that during the anodization process, surface defects are favored sites for pore nucleation. Furthermore, studies have shown that the presence of alloying elements in the Al substrate not only tend to reduce the rate of growth of the forming oxide layer, but also influence the structure of the oxide layer during the anodization process [12].

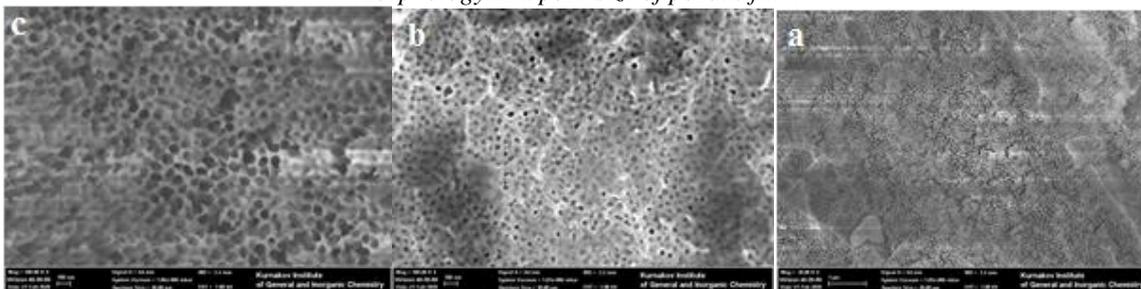
Morphology and pore size of porous film:

Figure 2 shows the morphology of the film anodised in temperatures, from 20 °C to 25 °C respectively.

Figure 3: SEM images of aluminium oxide films formed in (COOH)₂ at 20-25 °C.

The average pore diameter anodised in 20-25 °C was 100 nm. The pores were more irregular and smaller. This trend of result is similar with Shawaqfeh [13] which has reported that the formation of oxide film in phosphate based solution was increased at temperature to 25 °C, but it decreased when the temperature reached 30 °C. The effect of temperature on the formation of oxide is well-defined because it affects the rate of ion transport across the barrier layer, the oxide dissolution from the pore wall as well as the oxide surface and heat transport rates within the pore and the bulk electrolyte.

An increase in temperature resulted to an increase in the growth rate of aluminium oxide film formed in phosphoric acid electrolyte. At temperature 20°C to 25°C, the mass of oxide film increased. When the temperature rises up to 30°C, the mass of oxide film decreased. The effect of temperature on the formation of aluminium oxide film is noticeable because the temperature affects the rate of ion transport across the oxide layer, the oxide dissolution from the pore wall and heat transport rates within the pore and the electrolyte [13,14].

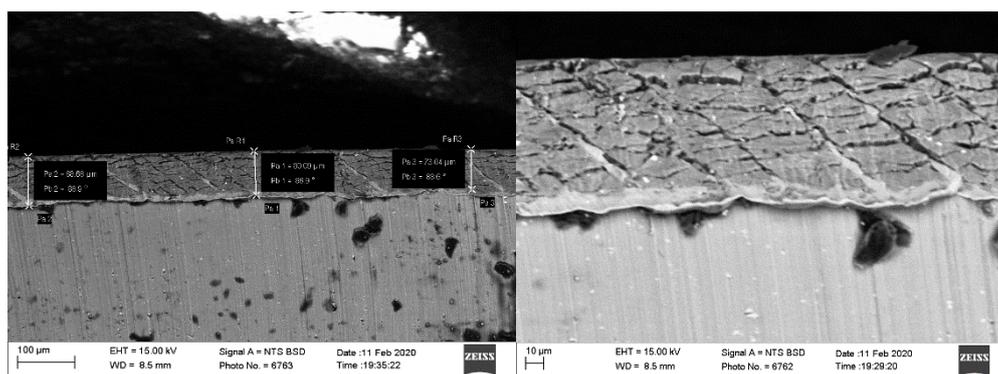


Figure 4: SEM image of cross sectional film anodised with temperature 20-25°C.

5. Conclusion

In summary, the nanostructured catalysts based on 3d metals (nickel) with a matrix of porous aluminum oxide was obtained. The morphological studies by SEM-EDX demonstrates a spongy structure with filament sizes of few nanometers is formed on the surface of the aluminum oxide matrix and this structure contains nanoparticles of nickel.

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