



Study on the Realization of High Specific Surface Area Al₂O₃ through Internal Anodization of Honeycomb Aluminum

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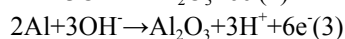
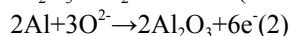
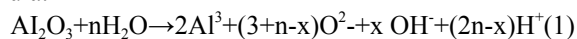
Abstract: In order to increase the specific surface area of the material, a porous alumina film was prepared in a sulfuric acid system using a honeycomb aluminum substrate and a constant voltage anodization method. The results indicate that at a lower voltage, internal anodization of honeycomb aluminum can be achieved. By extending the anodizing time to 8h, an anodized Al₂O₃ film with a maximum specific surface area of 10.147g / m² can be obtained. The pores are mainly mesoporous, with pores densely penetrating, and the diameter of the pores ranges from 9.42nm to 10.86 nm. This method has the characteristics of simple process. The anodized Al₂O₃ porous film has great application potential.

Keywords: honeycomb aluminum, anodizing, specific surface area

1. Preface

The interest of this research lies in the formation of a porous morphology in the anode film, which is very important in the surface treatment of aluminum^[1]. These porous membranes are mainly composed of amorphous alumina^[2-3], composed of an aluminum substrate, a barrier layer, and a porous layer^[4-5]. There are approximately cylindrical holes extending from the membrane surface to the barrier layer, each hole is located in a membrane cell structure of anodized aluminum, and the membrane cell group may form a regular pattern^[6-9]. At present, depending on the process, the thickness of porous AAO membranes is concentrated between 1 and 50 microns, the pore diameter can be between 5 and 200 nm, and the pore density can be between 109 and 1011 cm⁻²^[10]. Porous alumina as a stencil has the characteristics of low cost, high temperature resistance, good insulation, uniform and orderly pore distribution, and controllable size, so it has good application prospects.

According to the chemical reaction occurring on the electrode during anodization, it can be described by the following formula:



In the past research reports on porous alumina, there are types of anodized alumina and classification of anodizing methods. In the early stage, the main research on the preparation method of porous alumina film includes two methods, steady-state and non-steady-state. The steady-state anodization generally includes two methods, one is the soft anodization method, For example, in 1996 Masuda^[11] and others used a constant-pressure two-step soft anodizing method to prepare a highly ordered porous AAO membrane for the first time; the other is the hard anodizing method, compared with the previous method, the reaction process is fierce, the current density is large during the oxidation process, and the growth rate of the porous AAO film is fast, reaching 50 μm / h or more. A lot of heat, therefore, higher requirements are placed on cooling equipment. The hard-anodized AAO film, which can adjust the pore spacing in a wide range, can meet its application in the field of nanotechnology^[12]. Unsteady-state anodization refers to an oxidation process in which the oxidation voltage changes regularly or irregularly to break the balance between the growth rate and dissolution rate of the AAO film. Unsteady-state anodizing generally includes periodic anodizing and pulsed anodizing. For aluminum alloys with higher copper and silicon content, even if organic acids are added to the inorganic electrolyte, direct current oxidation is unlikely to obtain a good color oxide coating. During DC anodization, the initial passiveness of the anode is caused by polarization, which causes the anode surface to generate heat during the formation of a thick hard anode film. This issue is particularly important when trying to anodize high aluminum alloys, as the process ends in “burning”, And superimposing the alternating current in the form of ripple on the DC circuit can overcome the adverse effects brought by anodic polarization to a certain extent.

Using pulse current technology for anodization can overcome the above-mentioned disadvantages that coexist with

other anodizing processes. In 1960, Miller ^[13] used a unidirectional current pulse to anodize aluminum and its alloys at 60 Hz. In 1989, J. Kocich ^[14] anodized titanium alloy in a sulfuric acid-phosphoric acid aqueous solution at 0-10 ° C for 60 minutes, the pulse frequency was 1 Hz, the current density was 500 mA • dm⁻², and the potential range was 80- 200V. The periodic anodic oxidation refers to the preparation of AAO templates with periodic changes in shape and pore size by using an anodic oxidation method in which the current changes periodically and using an acidic solution as an electrolyte. By changing the periodic current parameters such as waveform, period, and amplitude ^[15], researchers have prepared AAO modes with periodic changes in channels, such as ratchets and circular channels. Compared with the pulse anodizing method, the periodic anodizing method can more accurately regulate the internal structure of the porous AAO film. Its appearance has made the porous AAO film with a special structure further applied in the application fields of nano-reactors, sensors, and photonic crystal expand.

In the past two decades, many scientists have used porous AAO membranes as templates to prepare various nano-wires ^[16] and nano-tubes ^[17], and also applied it to catalysis ^[18], filtration and biological functions ^[19], Photon and energy storage equipment ^[20], sensors ^[21-24] and other fields. In the future, with the continuous development of experimental techniques for the control of the internal structure of pores and the programming and functionality of the surface characteristics of porous AAO membranes, it is likely to further expand its application fields and achieve industrialization.

The purpose of the author's research is to experimentally analyze the internal morphology, specific surface area, and internal pore diameter of honeycomb aluminum after anodizing.

2. Materials and methods

2.1 Preparation of experimental materials

The purity of honeycomb aluminum is 99.5%, and the length, width and height are 30 * 25 * 2mm respectively. The reagents used in the experiment are Na OH (solid), nitric acid and sulfuric acid are analytically pure. The experimental water is distilled water.

2.2 Sample surface pre-treatment

Prepare a 30mm * 25mm * 2mm honeycomb aluminum core (99.99%), prepare a 5% NaOH (W / W) solution, and heat it with a water bath to control the temperature of the 5% Na OH solution to 40 ° C (ED (V.2) water bath Heating pot, JULABO, Germany) Dip honeycomb aluminum into Na OH solution with plastic tweezers and stir for 20 seconds; Take out the honeycomb aluminum, first immerse and rinse the honeycomb aluminum with water, and then rinse it with a distilled water bottle to wash the remaining Na OH solution (to remove surface oxides).

Prepare 19.5% HNO₃ (V / V) solution, then immerse the honeycomb aluminum in the HNO₃ solution and stir for 15s; remove the honeycomb aluminum, first immerse and rinse the honeycomb aluminum with water, and then rinse with a distilled water bottle to remove the remaining HNO₃ solution Wash clean (neutralize excess OH⁻).

Use a weighing paper to gently remove moisture from the surface of the honeycomb aluminum. The pre-treated honeycomb aluminum should be used for experiments as soon as possible.

2.3 Sample anodization

The pre-treated high-purity honeycomb aluminum core was oxidized under a 1A / 2.9V anodizing power supply (Zennium IM6 electrochemical workstation, Zahzer, Germany). The electrolyte was a sulfuric acid solution with a concentration of 0.3mol / L, and the 304 stainless steel plate The cathode uses a constant temperature water bath. The temperature is controlled at about 25 ° C, the oxidation voltage is 2.9V, the oxidation current is 20 ~ 300mA, and the oxidation time is 8h. The magnetic rotor speed is 750rpm (D-MAG HS7 type magnetic stirrer, IKA, Germany).

2.4 Observation and characterization of test samples

SEM observation: Remove the prepared porous anodized aluminum film, clean it with deionized water, and place it in a 30 ° C blast drying oven (electric constant temperature blast drying oven, Jinghong Experimental Equipment Co., Ltd., Shanghai). After drying, keep it in a sealed bag for future use. The cold-field emission electron microscope (SU 8220 scanning electron microscope, Calendar Hi-Tech Corporation, Japan) was used to observe the surface morphology of the alumina thin film; analyze the pore diameter and distribution order of the porous anodized alumina film. Scanning electron microscope photographs were used for random selection detection, and the thickness of the holes inside them was measured, and the average value was taken to reduce the error of the hole shape and the scanning electron microscope picture itself.

BET characterization: BET method was used to measure the specific surface area of honeycomb aluminum after fixed oxidation (ASAP2460, Mike Instruments, USA), and the isotherm adsorption branch was used to calculate the pore size

distribution data.

3. Results and discussion

Figure 1 shows the internal structure of honeycomb aluminum with a time of 4 hours and a voltage of 2.9v. It can be clearly seen from the figure that a porous oxide film is formed on the surface of honeycomb aluminum with a thickness of 380nm. Moreover, this membrane has a unique porous structure, which is composed of a thin and dense barrier layer at the bottom and a thick and loose porous layer thereon, but there are also a few cracks and hole defects [25]. There is a covering on the surface of the porous layer, which may be caused by the long-term electrolysis, and the reactions 1, 2, and 3 gradually balance. At the same time, each part that is in contact with the solution is reacting, but the reaction equilibrium is not reached at the same time, resulting in an overall inconsistency in the appearance of each pinhole. At the same time, observation under electron microscope also shows that under these conditions, it is difficult to form a regular regular hexagonal three-dimensional structure. After scanning the enlarged internal structure diagram, it can be seen that the inside of the formed porous membrane is a dense barrier layer, and the outer layer is composed of a porous layer, and has a unique interconnected structure.

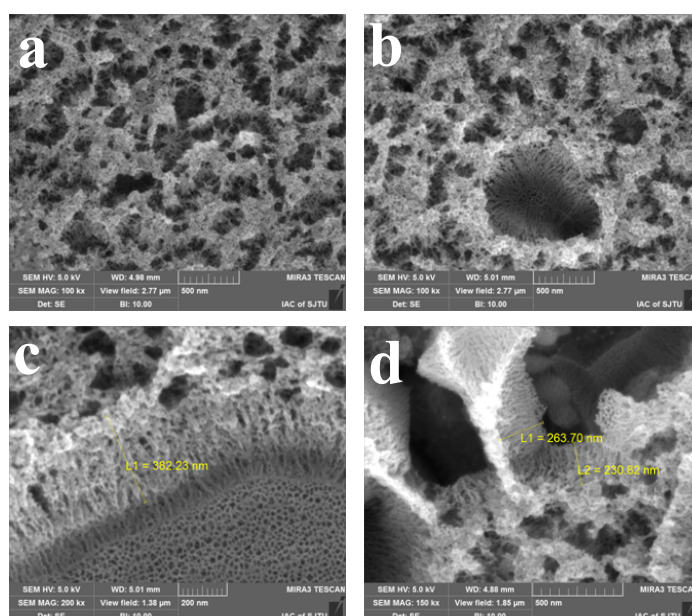


Figure 1. SEM image of anodized AAO film. Anodizing time was 4h

Figure 2 is the time-current graph of honeycomb aluminum for the first hour of 4 hours at a voltage of 2.9v. It can be found from Figure 2 that the current change trend at the beginning of the curve is that within half a minute of starting the current, the current drops and reaches a corresponding lowest point. At this time, a dense barrier layer with high resistance was formed on the aluminum surface. The trend after the curve can be clearly seen. The curve has significant peaks and troughs, which continue to the end of the reaction. It is generally believed that during the formation of porous anodic oxide films under acidic conditions, the curve of current density versus time can be divided into the following stages, the barrier layer formation stage, the microporous forming stage and the porous layer stable thickening stage [26]. The curve trend in the initial stage is consistent with the typical aluminum anodization, and the current fluctuations, the formation of micropores and the growth of the porous layer are unstable, because the low voltage is used in the preparation process, and the high field strength under high voltage is not available. It cannot provide sufficient power for the growth of alumina, and the pores cannot Very “good” growth, the direction of the hole is not perpendicular to the substrate, so a through hole is created.

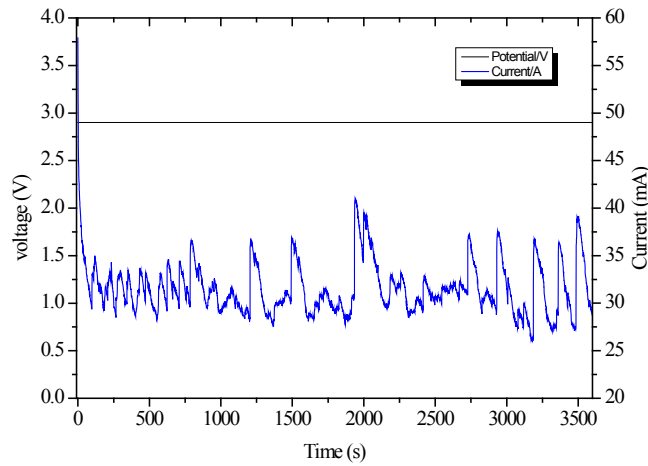


Figure 2. Time-current curve during oxidation. Anodizing voltage is 2.9V

The specific surface area of honeycomb aluminum before the experiment was $3 \sim 4 \text{ g} / \text{m}^2$. After 8 hours of anodization, the specific surface area reached $10.147 \text{ g} / \text{m}^2$. Prolonging the oxidation time is feasible to increase the specific surface area of the material. The oxidation time greatly affects the structure of honeycomb aluminum after oxidation at low voltage, which indirectly affects the adsorption performance of the material. The analysis of the BET measurement results also intuitively explains the reason for the increased specific surface area of the material. By observing the multi layer adsorption model, an accurate measurement of the specific surface area of the material was obtained.

Table 1 shows the pore size distribution of honeycomb aluminum with a time of 4 hours and a voltage of 2.9v. From the table we can see that the average pore diameter after adsorption for 4 hours is 10.68678 nm, the average pore diameter for desorption is 9.0693 nm, the average pore diameter for BJH adsorption is 9.2690 nm, and the average pore diameter for BJH desorption is 9.4275 nm. Figure 3 is the BJH desorption pore distribution map of the AAO membrane. It can be seen from the figure that a significant peak appears at 10 nm, indicating that the sample is optimally distributed at 10 nm.

Table 1. Pore size distribution of honeycomb aluminum after oxidation

Anodizing time	Adsorption average pore size	Desorption average pore size	BJH Adsorption average pore size	BJH Desorption average pore size
8h	10.8678 nm	9.0693 nm	9.2690 nm	9.4275 nm

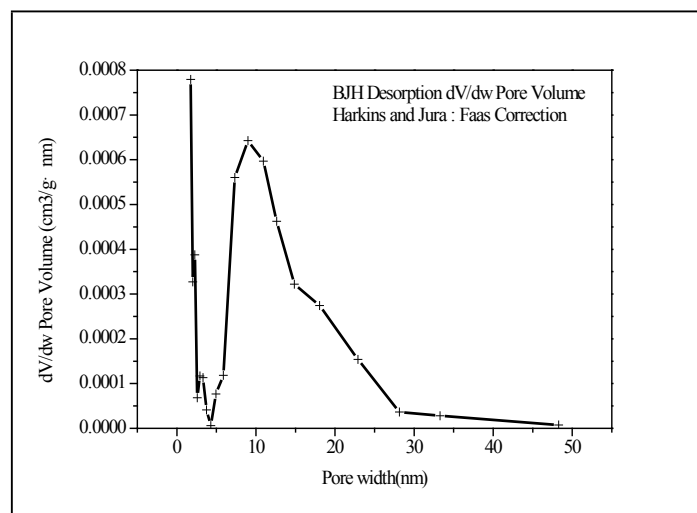


Figure 3. BJH desorption hole distribution

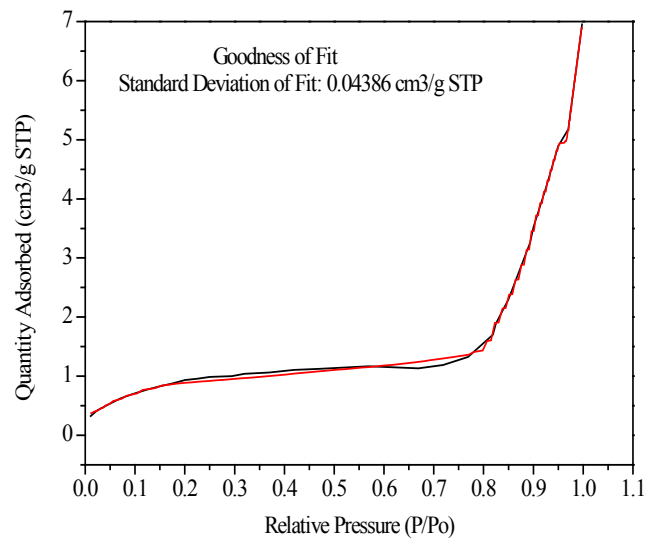


Figure 4. N₂ adsorption isotherm of AAO membrane

Fig. 4 is the N₂ adsorption isotherm of the AAO membrane. From the image, it can be concluded that the basic type of adsorption isotherm is category II ^[27], the line type is S-type, there is an inflection point in the low pressure region, and the inflection point indicates a single layer of saturated adsorption, and the number of subsequent layers is not limited. It exhibits typical reversible adsorption, which means that the mesoporous structure is dominant in the material.

4. Conclusion

Anodizing technology was used for internal anodizing of aluminum-based honeycomb materials, which increased the specific surface area. Alumina coatings were successfully prepared and the coatings were characterized. Through research, it is found that the film formed is more obvious at a voltage of 2.9v. It is composed of a thin and dense barrier layer at the bottom and a thick and loose porous layer thereon, and the porous layer is connected. According to the BET measurement results of the material after 8 hours, it can be known that prolonging the oxidation time is beneficial to increasing the specific surface area of the material, and in addition, the oxidation time also has a great influence on the oxidation of honeycomb aluminum. Future research suggests further exploring the influence of other factors on the anodizing process and considering the synthesis of aluminum-based alumina-coated composites to increase the material's adsorption performance.

5. Acknowledgement

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6. Research highlights

- 1 Anodization at low voltage was investigated.
- 2 Prolonged oxidation time will affect specific surface area
- 3 Connected holes are formed, increasing the specific surface area of the material
- 4 Low voltage anodization in sulfuric acid solution can cause reticulation

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