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ORIGINAL RESEARCH PAPER

Effect of Nanoporous Anodic Aluminum Oxide (AAO) Characteristics On Solar Absorptivity

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Abstract

Nanoporous anodic aluminum oxide (AAO) has been used in many different fields of science and technology, due to its great structural characteristics. Solar selective surface is an important application of this type porous material. This paper investigates the effect of nanoporous AAO properties, including; film thickness, pore area percentage and pore diameter, on absorption spectra in the range of solar radiation. The parameters were verified individually depending on anodization condition, and the absorption spectra were characterized using spectrophotometer analysis. The results showed that the absorptivity was increased with growth of the film thickness. Furthermore, increasing the pore diameter shifted the absorption spectra to the right range, and vice versa. The investigation revealed the presence of an optimum pore area percentage around 14% in which the absorptivity was at its maximum value.

Keywords: *Film thickness, Nanoporous Anodic Aluminum Oxide (AAO); Pore diameter; Pore area percentage, Solar absorptivity.*

1. Introduction

Nanoporous anodic aluminum oxide (AAO) has been produced for more than a century by anodizing of aluminum [1]. It contains close-packed array of columnar hexagonal cells with a central pore normal to the substrate [2]. Fig. 1 shows a schematic presentation of AAO. It is well known that AAO films, which is produced by two-step anodization process, comprise a high structural regularity [3]. The produced nanoporous film would attain characteristics, such as; high aspect ratio, high pore density, uniform pore size, and uniform nanopores dispersion [4]. The pore diameter (10–500 nm), inter-pore spacing (20–1000 nm), pore ordering, film thickness (50–200 μm), and other structural features of AAOs would be controlled by manipulating the anodizing operational parameters. The latter parameters are included of composition and pH of electrolyte, anodizing potential, anodizing time, temperature and etching methods [1, 5]. High pore density, thermal stability, and cost effectiveness are the other advantages of AAO films as compared to other porous materials [6]. Because of these properties, in recent decades, AAO films have been extensively used as a template for fabricating of nanotubes, nanowires, nanorods, nanorings, nanocones, nanomembranes, and nanoparticles [7].

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AAO film has attracted considerable attention in diverse applications in the fields of molecular separation, catalysis, energy storage, drug delivery, integrated circuits, chemical sensing, medicine, military, biomedical, optoelectronics, and magnetic recording [6, 8-10]. The current AAO studies focus on the types of pore structure, high-speed film growth, controlling the pore diameter and its uniformity, interpore distance and thickness, as well as new applications of AAO films [1].

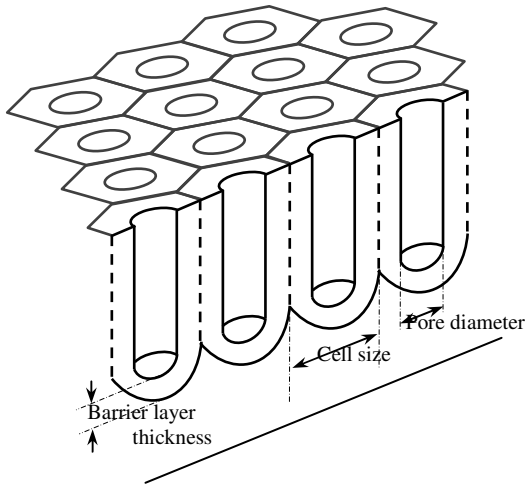


Fig. 1. a) 3D schematic presentation of nanoporous AAO film.

The application of nanoporous AAO for production of solar selective surfaces goes back to about 1980. However, in recent years, it has drawn the attentions more due to increasing the solar energy usage. Recent investigations deal mostly with deposition of different metals (e.g. Ag, Ni, Cu, etc.) on the thin AAO film with the aim of improvement of optical properties [11-14]. Nevertheless, there are few studies centered on the optical properties of bare AAO film in the literature [15-18]. Moreover, high-purity aluminum (more than 99.9%) has been used in most of these researches. An important disadvantage of high-purity aluminum is its relatively high price, and its limited size. On the other hand, aluminum alloys with a lower purity are cheap and easily available [5].

The main aim of this paper is to investigate the effect of nanoporous AAO properties (i.e. film thickness, pore area percentage and pore diameter) on solar absorptivity. In the study, these parameters are changed individually by manipulating the anodization condition, and then the absorption spectra are characterized using spectrophotometer analysis. The paper focuses on relatively thicker nanoporous AAO films, produced by two-step anodizing of commercially aluminum alloy 1050.

2. Experimental

The AAO films were fabricated using the two-step anodization of 1050 aluminum alloy sheets (1mm thickness). The aluminum sheet was initially cut into 1cm×5cm pieces and degreased in acetone, without further thermal treatment or chemical polishing. The first anodization step was then carried out on the aluminum specimen, suspended in the electrolyte as anode, under constant current density of 5mA/cm^2 for 10 h. Another aluminum specimen was used as cathode. Oxalic acid and sulfuric acid solutions (0.4M concentration) were used as electrolyte, and the electrolyte temperature was controlled at 5, 15, and 35˚C using cold water circulation bath. Since the anodization was an exothermic process, the temperature distribution over specimen was kept constant by vigorous stirring the electrolyte bath.

The formed AAO film was chemically removed by immersing the specimen in 0.4M phosphoric acid solution at 50˚C for 1 h. The second anodization step was subsequently conducted at various times under the same condition mentioned before for the first step, to produce the final AAO film with a regular nanopore array. Some final samples were immersed in 0.2M phosphoric acid at 40˚C and appropriate etching time to widen the pores. Finally, the specimens were rinsed several times with deionized water and then dried in air. The schematic diagram of experimental setup is shown in Fig. 2.

Pore diameter and percentage of pore area were determined by analyzing the SEM images of samples using FE-SEM (MIRAII TESCAN) and Motic Image Advanced 3.2 software. At first, each image was calibrated in the software with its scale bar. Then, diameter of at least 200 pores was measured with ruler of the software. The obtained pore diameter for each sample was the average of these measurements. Pore area percentage was determined automatically by the software, according to the color difference between the pores and AAO surface. Spectral reflection of each samples determined using spectrophotometer (Varian-Cary500) in the range of solar radiation (200-

3000 nm). Solar absorptivity of the samples were calculated using the following equation [19].

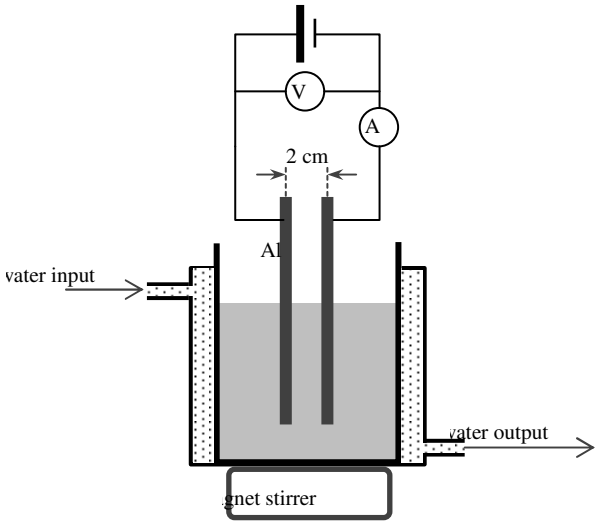


Fig. 2. Schematic illustration of experimental setup

$$\alpha_s = \frac{\int_{0.35}^{2.5}[1 - R(\lambda)]I(\lambda)d\lambda}{\int_{0.35}^{2.5} I(\lambda)d\lambda} \quad (1)$$

where *R(λ)*, and *I(λ)* are the reflection intensity and solar radiation intensity at the wavelength λ, respectively.

3. Results and discussion

Table 1 summarizes the anodization conditions and properties of produced nanoporous AAO films including pore diameter, percentage of pore area and solar absorptivity. The first three test runs in this table deal with the effect of film thickness on solar absorptivity. Test runs 3, 4, and 5, consider the relation between pore area percentage and solar absorptivity. The last three test runs, study the effect of pore diameter on the solar absorptivity, where sulfuric acid was considered as their electrolyte. Two different acids were selected in this study as pores' diameter of AAO film obtained in sulfuric acid were smaller as compared those produced in oxalic acid [20].

3-1. Effect of film thickness on solar absorptivity

The second step anodization time varied only the AAO film thickness. Therefore, the effect of anodization time (in fact film thickness) on solar absorptivity of AAO films, produced at various durations (test runs; 1, 2, and 3), was investigated. Left hand of Fig. 3 illustrates these results as the absorptivity of the nanoporous AAO films versus the wave length of radiated light on the surface of mentioned samples. According to the table 1, AAO film on sample 1 is thinner than sample 2. Sample 3 has thickest film among these three samples. Digital image of these samples presented in the right hand of Fig. 3.

As it is seen in the Fig. 3, absorption spectra of sample 1 (with thinnest AAO film) placed under two other curves. In addition, the upper curve belongs to the sample 3 (with thickest AAO film). Therefore, it is conclude that, increasing the film thickness by the increasing of anodizing time, leads to enhancement of absorption over the solar spectra range. Similar result was obtained in the study of Santos et al. for thinner AAO films [18]. However, absorption growth is more vigorous for shorter wavelength, especially for λ<1200nm in this study. Therefore, it is generally concluded that the solar absorptivity increases by thickening of the film. Indeed, more penetrated beams are trapped by thicker AAO film due to its deeper medium. This concept can be used in the volumetric solar receiver, in which the porous film absorbs the solar concentrated radiation in the depth of their structure, and transferring the heat to the working fluid. Decreasing the heat loss by temperature reduction on the irradiated side of the volumetric solar receiver is an important feature [21], where it looks the thick nanoporous AAO films can play this role properly.

3-2. Effect of pore area percentage on solar absorptivity

Pore area percentage depends straightly on the pore density (number of pores in a certain area). It has been reported that pore density increases by rising the anodization temperature [17]. Therefore, the effect of anodization temperature on the pore area percentage and consequently on the absorptivity of AAO film was studied. The test runs 3, 4, and 5 in Table 1

Table1. Anodization conditions and properties of produced nanoporous AAO films

Test run	2nd step time (h)	Electrolyte	Anodization temperature (˚C)	Etching time (min)	Pore diameter (nm)	Pore area %	Solar absorptivity
1	2	Oxalic acid	35	-	27.07 ± 2.98	23.04	0.3249
2	4	Oxalic acid	35	-	27.46 ± 3.11	23.25	0.4376
3	6	Oxalic acid	35	-	27.83 ± 3.03	23.41	0.5529
4	6	Oxalic acid	15	-	27.15 ± 3.70	14.62	0.6192
5	6	Oxalic acid	5	-	27.62 ± 3.43	8.13	0.5827
6	6	Sulfuric acid	35	-	14.78 ± 1.58	4.25	0.4213
7	6	Sulfuric acid	15	10	17.39 ± 1.60	4.04	0.4110
8	6	Sulfuric acid	5	20	23.54 ± 1.27	4.11	0.3932

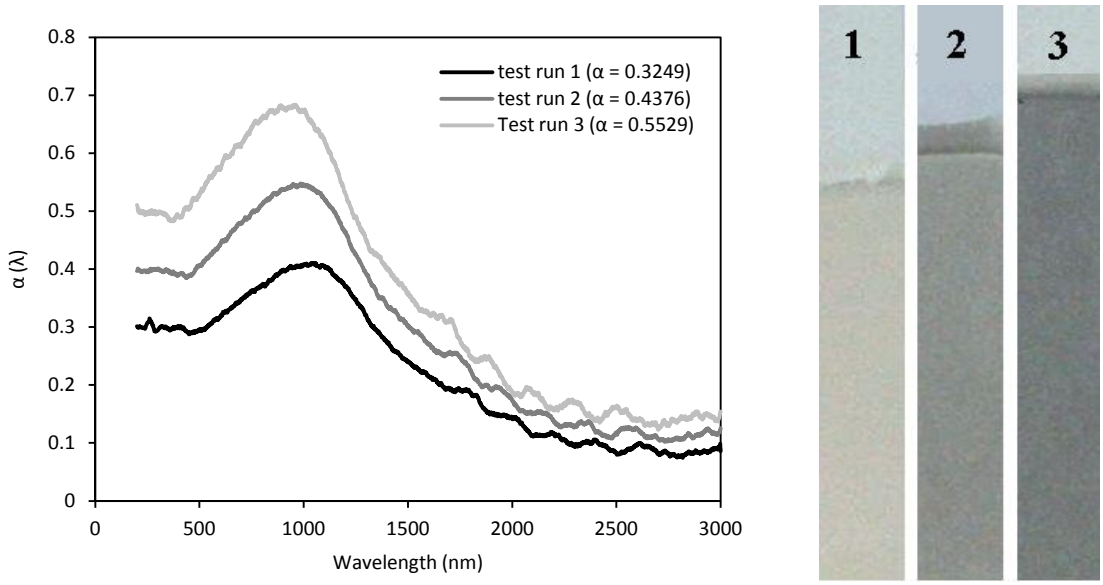


Fig. 3. Effect of nanoporous AAO film thickness on absorption spectra.

present this effect in which a reduction in pore area percent is observed from 23.41% to 8.13% when the temperature is reduced from 35˚C to 5 ˚C. Digital images of samples 3, 4, and 5 presented in the right hand of Fig. 4. Central part of Fig. 4 shows the SEM images of these samples. Absorptivity of the nanoporous AAO films produced on samples 3, 4, and 5 versus the wave length is presented in the left hand of Fig. 4. Fig. 4 shows that decreasing the pore area percentage from 23.41% to 14.62% (correspond to the temperature reduction from 35˚C to 15˚C) leads to an increase of the absorption intensity in the most wavelengths. In this case, the, absorptivity increases from 0.553 to 0.619 . This observation is confirmed by the results presented by Shih et al. study [17]. In fact, high reflection characteristic of Al substrate has a great influence on the reflection spectra of the AAO film [15]. Considerable portion of penetrated beams could reach to the Al substrate for the AAO film with large void fraction. These beams are reflected toward the film surface, and a portion of them refracted to the outside of the film. The refracted beams to the outside of AAO are reduced by the pore area percentage reduction, leading to increasing of absorptivity. Nevertheless, absorption spectra of test run 5 reveals that, further decreasing of pore area percentage may have

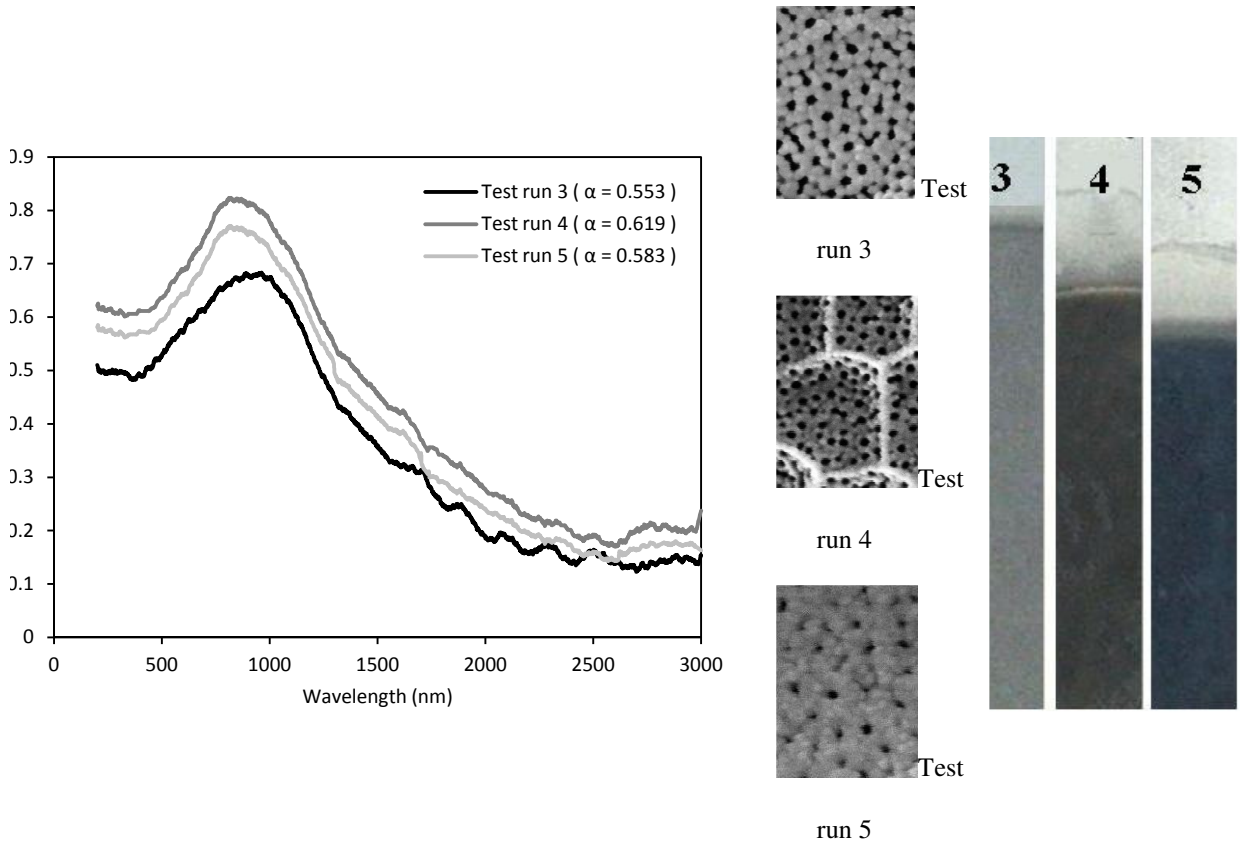


Fig. 4. Effect of pore area percentage on absorption spectra

opposite effect. Further decreasing of the pore area percentage from 14.62 to 8.13 reduces the penetrated beams or absorptivity from 0.619 to 0.583. In fact, in this case, most portions of incident beams on the AAO surface are reflected from it.

3-3.Effect of pore diameter on solar absorptivity

Pores diameter could be increased by etching of the produced AAO in phosphoric acid solution. The surface widening of pores occurs effectively at longer etching time, leading to an increase in pores' diameter. Nevertheless, as the diameter of pores increases, the percentage of pore area also increases simultaneously. This fact has been neglected by the researches which have investigated the effect of pore diameter on the optical properties of AAO film, such as the work of Huang et al. [4]. Therefore, etching should be carried out on the AAO film with lower pore density. This strategy causes that the pore area percentage remains constant after the etching step. In fact, more etching time needs less pore density or pore area percent. Pore density could be decreased by decreasing of the anodization temperature. Anodization condition defined for test runs 6, 7, and 8 obviously indicates this strategy. It is clear from Table 1 that with the mentioned strategy the pore diameter is increased considerably from 14.78 to 23.54 nm, with decreasing the temperature from 35 to 5 ^{0}C and increasing the etching time from 0 to 20 min. Right hand of Fig. 5 shows digital images of samples 6, 7, and 8. SEM images of these samples presented in the central part of this Fig. Absorptivity of the samples 6, 7, and 8 versus the wave length is presented in the left hand of Fig. 5. As it seen, peak of absorption spectra shifts to the right with increasing of pore diameter. This result implies the

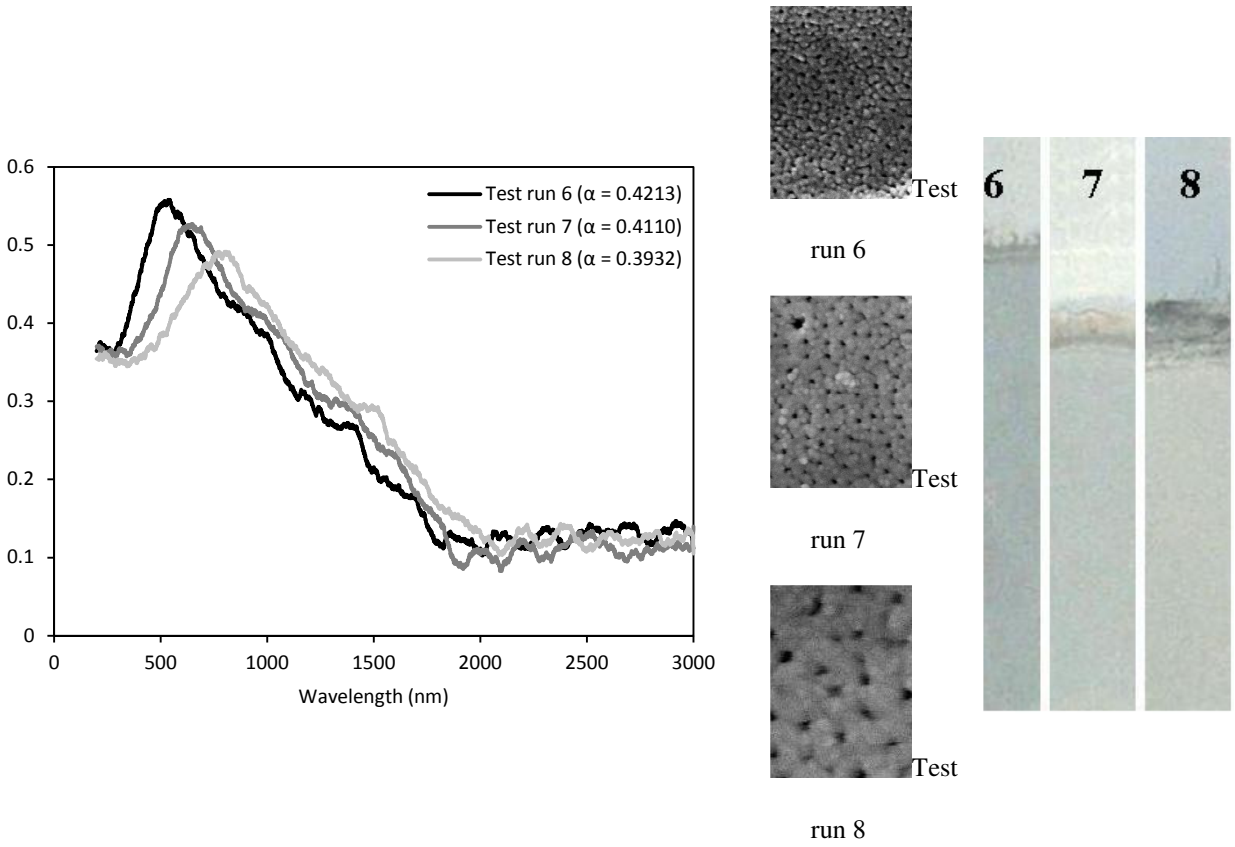


Fig. 5. Effect of pore diameter on absorption spectra

straight dependence between the peak of absorption spectra and the pore diameter. Furthermore, increasing the pore diameter leads to a slight reduction in the absorption spectra from 0.4213 to 0.3932. This reduction is more apparent for shorter wavelengths, since they penetrate more to AAO film.

4. Conclusion

AAO films with various structural features were produced on 1050 Aluminum alloy by a two-step anodization at different conditions. The main objectives of the paper were to investigate the effects of film thickness, percentage of pore area, and pore diameter on solar absorptivity. These properties were investigated individually to avoid their interactions. The film thickness and pore area percentage were changed by variation of the anodization time and electrolyte temperature, respectively. The pore diameter was altered by varying etching time and electrolyte temperature. The results showed that, increasing of the film thickness shifted the absorption spectra to the higher value, leading to growth of solar absorptivity. Furthermore, an optimum pore area percentage could be characterized (14.6% in this study) in which the absorptivity had a maximum value. At last, it was found that the peak of absorption spectra depended on the pore diameter. In this case, decreasing of the pore diameter shifted the absorption spectra curve to the left, and vice versa.

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