

Article

Study on Parameter Correlation of Thickness and Performance of Anodizing Film on 6061 Aluminum Alloy Frame in High Energy Laser System

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Abstract: As stray laser light is difficult to avoid in high-energy laser systems, it is of great significance to improve the laser damage resistance of the aluminum alloy frame anodizing film system. In this paper, the effects of anodic oxidation parameters on the thickness and performance of 6061 aluminium alloy anodic oxide composite film systems are investigated combining experiments and simulations. The thickness of the oxide film is calculated theoretically, and the simulation model is established. Then the effects of anodizing parameters and the reasons are analyzed. After characterizing the surface quality and laser damage resistance of the oxide film, the influence of anodizing parameters is summarized. This paper enables advance calculations of film thickness within a certain range, combined with the film properties, to provide a reference for the laboratory preparation of 6061 anodizing films and the preparation of structure-specific composite film systems based on the film.

Keywords: 6061 aluminum alloy; anodizing; film thickness calculation; laser damage resistance



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1. Introduction

High-energy laser systems have a wide range of applications in both military and civil fields. It is of great significance to ensure that high energy laser systems can work stably. However, stray laser is unavoidable in high energy laser system. One of the main problems in high energy laser systems is the damage of optical elements caused by system pollutants. When the high-energy laser passes through the optical element, the pollutant particles on its surface can produce damage of about five times its own size, which makes the laser damage threshold drop sharply. Therefore, it is very important to maintain the cleanness of the high-energy laser system [1]. Stray light is inevitable when the high energy laser passes through the potassium dihydrogen phosphate crystal (KDP) crystal and can cause damage to the aluminium alloy frame of the system, resulting in spatter particles and secondary contamination that can affect the stability of the high energy laser system [2]. Whether the frame structure has good resistance to laser damage is an important factor in determining the operation of high-energy laser systems. Therefore, the preparation of laser resistant films and the damage mechanism have been studied by scholars for many years.

In 2015, Bellum et al. investigated that a combined $\text{HfO}_2/\text{SiO}_2$ eleven-layer film could be used in laser protection. The $\text{HfO}_2/\text{SiO}_2$ film was prepared by vacuum ion sputtering and then tested for resistance to laser damage under laser irradiation with wavelengths of 527 nm and 1054 nm. The results showed that the laser damage threshold could be effectively increased [3]. In 2016, Bellum et al. improved the previous film system by replacing two surface layers with Al_2O_3 to improve the laser damage resistance. The results showed that the newly prepared film can resist the laser with an energy density of 7 J/cm^2 [4]. Chai et al. improved the $\text{HfO}_2/\text{SiO}_2$ film system using a pre-alignment method to prepare $\text{HfO}_2/\text{SiO}_2$ highly reflective films on the substrate with prefabricated pits while

incorporating a suture layer formed with plasma assisted deposition. The results showed that the composite film layer with the suture layer is more stable against laser damage and has fewer internal cracks compared to the film without the suture layer. The suture layer could also effectively improve the overall mechanical stress of the film system, reduce multilayer deformation and reduce the effect of substrate prefabrication surface defects. Therefore, especially for substrates with low surface quality, the suture layer could make the surface smoother and reduce the probability of damage [5]. Geisler et al. proposed a light absorption model of porous anodic oxide layer. The thickness and surface quality of the oxide film are measured by the intensity of the light beam passing through the oxide layer and reflected back from the surface and bottom [6]. The effect of different surface treatment processes on the laser resistance of aluminum alloys was studied by Shuang Shi et al. The laser damage was compared under various surface treatment processes such as no surface treatment, mechanical polishing, black anodizing, hard anodizing, chemical nickel plating, passivation and microarc oxidation. It was shown that the laser damage threshold, by means of nickel plating, anodizing and microarc oxidation, was directly related to the thickness, and the damage threshold tended to stabilize when the thickness exceeded 10 μm . The surface obtained by microarc oxidation and passivation was more resistant to laser damage, but the study also pointed out that the porous structure of anodic oxidation is conducive to the deposition of particles and light absorption [7].

The optical properties of the aluminum anodized film are closely related to the thickness of the film [8,9], so the thickness needs to be precisely controlled. During the anodic oxidation process, many factors affect the properties of the film, such as current density, feeding method, time, type of electrolyte, bath temperature and properties of the aluminum alloy itself. Only by considering all these factors can we achieve the control of the film properties [10]. Sakairi et al. studied the relationship between the film thickness and temperature and prepared the oxide film with controllable thickness by controlling the temperature [11]. In 2013, Sakairi et al. applied solution flowing micro drop cell (Sf MDC) to local anodic oxidation to form porous aluminum oxide film with controllable thickness and width. The porous aluminum anodic oxide film with controlled area and thickness can be formed by controlling the substrate temperature and the number of repetitions [12]. In 2011, Ionita et al. studied the morphology, structure and characteristics of anodic oxide films at high current densities and concluded that the surface morphology of oxide films was rougher and the film was more hydrophilic at higher current densities. The corrosion resistance of oxide films showed a certain functional relationship with the oxidation current density, and the corrosion resistance increased with voltage. However, at particularly high current densities, the corrosion resistance decreased significantly [13]. Chiang et al. controlled the growth rate of the film at several nanometers per minute by exposing the substrate to laser irradiation in the anodic oxidation process to achieve accurate thickness control [14]. In 2018, Miyakita et al. studied the morphology of phosphoric acid anodizing film under different voltages. The results showed that the anodizing of aluminum magnesium lithium alloy in phosphoric acid solution would produce a white film and become thicker with the increase of voltage [15]. In 2020, Rashid et al. indicated that temperature and time play a very important role in the anodic oxidation process. The interaction between variables was not obvious [16].

The main problems of previous studies are as follows. The thickness of anodic oxide film is affected by various factors, and most of the existing studies are qualitative studies, and how to achieve accurate thickness control is rarely studied. The cost of existing means of precise thickness control is too high to realize large-scale application. The study of film properties in anodic oxidation is mainly qualitative. The specific analysis of the influence of various factors on the oxide film performance is relatively lacking, and the influence on the composite film or laser damage resistant films is rarely studied. Therefore, the parameter correlation of the film thickness in the anodizing process is studied, and a simulation model is established to realize the advance calculation of the film thickness in the anodizing

process, and the parameter correlation of the surface quality and laser damage resistance is studied.

2. Materials and Methods

2.1. Materials and Experimental Scheme

The composite film system in this study is a three-layer structure with a dense barrier layer, a porous alumina layer in which CdSe nanoparticles are deposited and a silicon oxide layer from bottom to top. The specimens are 6061 aluminum alloy, 20 mm × 20 mm × 3 mm, polished to a mirror finish to improve the film quality and to minimise the variation between specimens to reduce experimental error. The specimens are anodised after degreasing, alkali etching and neutralisation. The anodising bath consists of sulphuric acid with aluminum powder and a small amount of nano-scale silicon oxide particles, which enhance the toughness of the oxide film and reduce the possibility of cracking [17]. After the anodic oxidation process, the film is used as a template for the deposition of light-absorbing CdSe particles by immersing the specimen in an electrolytic deposition bath. Finally, the specimen is immersed in a high temperature silicon solution for sealing the holes and prevent the CdSe deposited particles from leaking out, improving the wear and corrosion resistance of the film.

The control group anodizing parameters are as follows: sulphuric acid concentration of 200 g/L, anodizing time of 60 min, power supply of 2 A/dm² DC and temperature of 10 °C. The parameters for the time group are 20 min, 30 min, 40 min, 60 min, 90 min and 120 min. The parameters for the temperature group are 10 °C, 15 °C, 20 °C and 25 °C. The current density groups are 1.5 A/dm², 2.0 A/dm², 3.0 A/dm² and 4.0 A/dm². Half of the specimens complete the subsequent deposition sealing process and half are anodised only.

2.2. Film Thickness Calculation

The thickness of the anodic oxide film was calculated theoretically before the experiment. An anodic oxidation is an electrochemical process and follows the relevant electrochemical laws. According to Faraday's first law, the amount of substance produced by an electrode reaction is proportional to the amount of electricity flowing through that electrode.

$$\frac{m}{Q} = k \quad (1)$$

where m is the mass of the substance produced by the electrode reaction, Q is the amount of electricity flowing through the electrode and k is a constant. In the process of anodizing, without taking into account the dissolution of sulphuric acid, efficiency and other factors, every two aluminum atoms oxidised will produce one aluminum oxide molecule. The amount of electricity flowing through the anode is directly related to the film thickness. With a constant current power supply, the current density J can be considered as a constant.

$$Q = J \cdot S \cdot t \quad (2)$$

where J is the current density, S is the anode plate area and t is the anodizing time. According to Faraday's second law, the mass of aluminum oxide generated on the anode during the anodizing process is proportional to the product of the electricity passing through the anode and the gram equivalent of the aluminum oxide. That is,

$$m = \frac{1}{F} \cdot \frac{A}{n} \cdot Q \quad (3)$$

where F is Faraday constant, A is the molar mass of alumina, n is the number of electrons required to produce an alumina molecule and $\frac{1}{F} \cdot \frac{A}{n}$ is the electrochemical equivalent k , which has a value of about 1.7619×10^{-4} g/C. The Equation (3) can be written as

$$m = k \cdot J \cdot S \cdot t \quad (4)$$

The relationship between mass and film thickness is shown in Equation (5).

$$m = \rho \cdot S \cdot \delta \quad (5)$$

where ρ is the density of aluminium oxide in g/cm³ and δ is the film thickness. The oxide film thickness is shown in Equation (6).

$$\delta = \frac{k}{\rho} \cdot J \cdot t \quad (6)$$

Equation (6) is the theoretical thickness under constant current conditions without consideration of current efficiency, sulphuric acid dissolution and porosity. In practice, the main factors affecting film thickness are current efficiency, sulphuric acid dissolution and porosity. Current efficiency affects the actual number of electrons involved in the reaction and porosity affects the true area of the reaction. The current efficiency in the anodizing process of aluminum alloys is shown in Equation (7).

$$\eta = \frac{(6 \times F) \cdot (m_1 - m_2)}{Q \cdot M_{\text{Al}_2\text{O}_3}} \quad (7)$$

where η is the current efficiency, m_1 is the weight of the specimen after anodising, m_2 is the mass of the specimen after removal of the oxide film and $M_{\text{Al}_2\text{O}_3}$ is the molar mass of the aluminium oxide molecule.

After preliminary experiments, the current efficiency in relation to sulphuric acid concentration, temperature, time and current density within the range involved in this study is shown in Figure 1. The other three variables in each figure are the reference values in this study, i.e., sulphuric acid concentration of 2 mol/L, temperature of 15 °C, oxidation time of 60 min and current density of 2 A/dm².

The anodic oxide film thickness can be calculated as shown in Equation (8).

$$\delta_1 = \frac{\delta \cdot \eta}{1 - P} - \delta_s \quad (8)$$

where P is the porosity. In this study the oxide film pore structure is similar, and the porosity is about 30%. δ_s is the thickness of alumina dissolved by sulphuric acid. Experimentally, the rate of oxide film dissolution in sulphuric acid at 15 °C is measured to be approximately 1.5 µm per hour. In summary, the calculated film thickness of the oxide film can be derived.

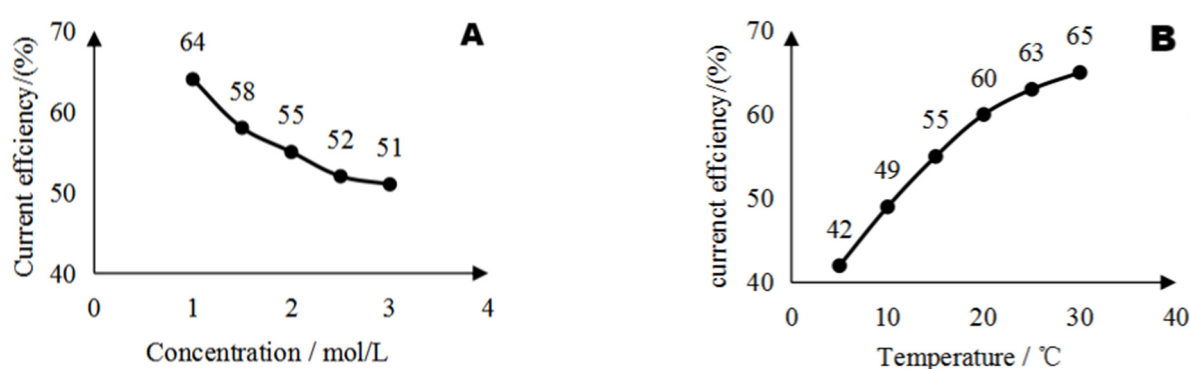


Figure 1. Cont.

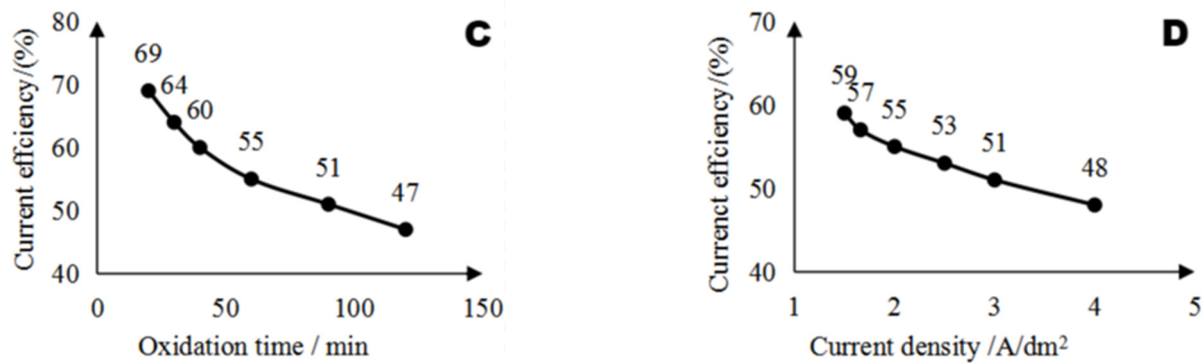


Figure 1. Relationship between current efficiency and different factors. (A) The relationship between current efficiency and concentration; (B) The relationship between current efficiency and temperature; (C) The relationship between current efficiency and oxidation time; (D) The relationship between current efficiency and current density.

2.3. Simulation Model Establishment

The current distribution and film thickness of the anodic oxidation process were simulated using the secondary current distribution interface in the electrochemical module of Comsol. In this study, the 6061 aluminum alloy specimen size was 20 mm × 20 mm × 3 mm, the oxidation tank was a 10 L beaker with an internal diameter of 255 mm, the sulphuric acid solution height was 260 mm and the cathode plate size was 100 mm × 100 mm × 3 mm. A simplified model is shown in Figure 2.

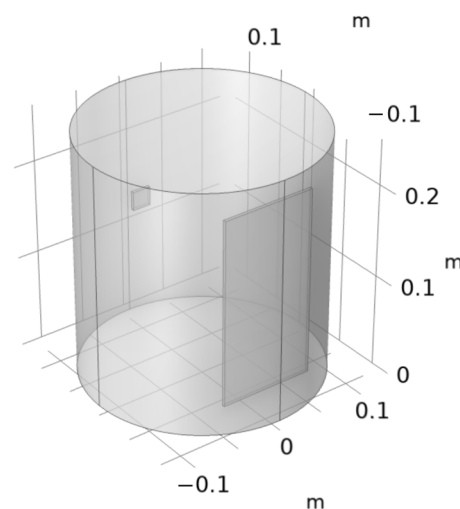


Figure 2. Simplified geometric model.

The other main parameters of the model are shown in Table 1. This study does not consider the actual porosity of the alumina film layer in the simulation and only uses the porosity data to correct the film density—i.e., the density of the oxide film after considering the porosity is 2729 kg/m³. The alumina porous film layer has a high resistance and the film resistance must be set. The actual resistance of the oxide film is shown in Equation (9).

Table 1. Other parameters of simulation model.

Solution Conductivity	Alumina Density	Porosity	Film Resistivity
55 S/m	3970 kg/m³	30%	$4 \times 10^3 \Omega \cdot \text{m}^2/\text{m}$

This study does not consider the actual porosity of the alumina film layer in the simulation and only uses the porosity data to correct the film density—i.e., the density of the oxide film after considering the porosity is 2729 kg/m^3 . The alumina porous film layer has a high resistance, and the film resistance must be set. The actual resistance of the oxide film is shown in Equation (9).

$$R_{\text{film}} = \frac{S_0 + \Delta s}{\sigma_{\text{film}}} \quad (9)$$

where s_0 is the reference film thickness, Δs is the amount of film thickness variation and σ_{film} is the film resistivity. The anode voltage variation is shown in Equation (10).

$$\Delta\phi_{s,\text{film}} = R_{\text{film}} \cdot i \quad (10)$$

The film thickness is controlled with Equation (11).

$$\Delta s = \sum_j \frac{(c_{d,j} - c_{d,j,0}) \cdot M_j}{\rho_j} \quad (11)$$

where $c_{d,j} - c_{d,j,0}$ is the amount of substance of the product, M_j is the molar mass of the product and ρ_j is the density of the product.

The geometry of the model is relatively simple and is meshed using a free tetrahedral mesh, with mesh refinement for the anode. The results of the meshing are shown in Figure 3.

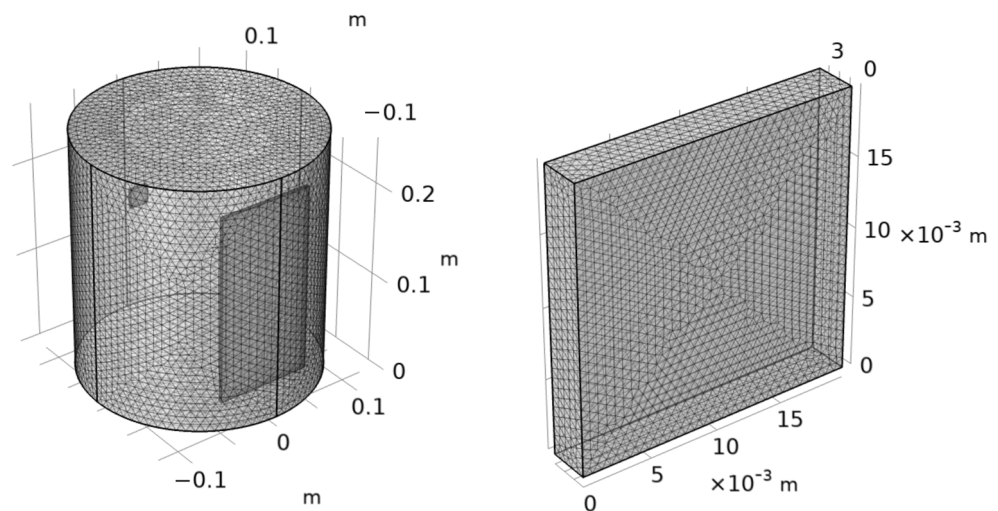


Figure 3. Model meshing.

2.4. Laser Experimental Parameters and Detection Methods

Laser damage tests were performed on the specimens using a laser with a spot diameter of $275 \mu\text{m}$ and a wavelength of 1064 nm . Single-pulse lasers with energy densities of 0.3 , 0.5 and 1.0 J/cm^2 were used to impact the specimens. The laser irradiation locations were characterized using scanning electron microscopy and white light interferometry.

3. Parameter Correlation of Oxide Film Thickness

Anodic oxidation was carried out in 2 mol/L sulphuric acid solution at a controlled temperature of $15 \text{ }^\circ\text{C}$ with a temperature difference of no more than $1 \text{ }^\circ\text{C}$ before and after the experiment and an oxidation time of 1 h . The current densities were 1.50 , 1.67 , 2.00 , 3.00 and 4.00 A/dm^2 . After the calculation and experiment, the thickness of the oxide film are shown in Table 2.

Table 2. Calculated and measured film thickness with different current density.

Current Density	Calculated Thickness	Measured Thickness
1.50 A/dm ²	18.74 µm	19.5 µm
1.67 A/dm ²	20.74 µm	20.2 µm
2.00 A/dm ²	24.92 µm	22.6 µm
3.00 A/dm ²	34.61 µm	30.6 µm
4.00 A/dm ²	43.47 µm	42.0 µm

By comparing the theoretical calculation results with the actual experimental results, it was found that at low current densities, the difference between the calculated thickness and the measured thickness is small, while at high current densities, the difference is relatively large. This is mainly due to the fact that as the current density increases, the surface temperature of the oxide film increases, and it is difficult to ensure a stable surface temperature. The increase in surface temperature causes the sulphuric acid to dissolve the alumina at a faster rate. Meanwhile, at higher current densities, significant oxygen bubble formation can be observed on the anode surface, and the current efficiency is reduced. In the current density range of 1.5 A/dm² to 4 A/dm²—i.e., the range of current densities commonly used for sulphuric acid anodizing, advance calculation of film thickness can be achieved.

The anodizing times for the time groups were 20, 30, 40, 60, 90 and 120 min. After calculation and experiment, the oxide film thicknesses are shown in Table 3.

Table 3. Calculated and measured film thickness with different oxidation time.

Oxidation Time	Calculated Thickness	Measured Thickness
20 min	9.92 µm	10.4 µm
30 min	13.75 µm	12.2 µm
40 min	17.13 µm	17.8 µm
60 min	24.92 µm	22.6 µm
90 min	32.43 µm	33.4 µm
120 min	39.62 µm	37.8 µm

After comparing the measured film thickness with the calculated film thickness, the maximum difference between the predicted and actual values in the range of 20 min to 120 min is 1.98 µm, which can be considered as achieving advance calculation of the oxide film thickness considering the error during the actual preparation.

The anodizing temperatures for the temperature groups were 10, 15, 20, 25 and 30 °C. After calculation and experiment, the oxide film thickness is shown in Table 4.

Table 4. Calculated and measured film thickness with different temperature.

Temperature	Calculated Thickness	Measured Thickness
10 °C	20.72 µm	21.4 µm
15 °C	23.44 µm	22.6 µm
20 °C	25.71 µm	26.3 µm
25 °C	27.07 µm	27.9 µm
30 °C	27.97 µm	28.7 µm

After comparison, the maximum difference between the predicted and actual values is 0.84 µm in the range of 10 °C to 30 °C. It can be assumed that the advance calculation of oxide film thickness can be achieved in this temperature range.

In an ideal model, the thickness of the anodic oxide film is proportional to the current density. However, in the actual preparation process, the current efficiency tends to decrease as the current density increases. The relationship between current density and current

efficiency is brought into the model to obtain a predictive model of anodic oxide film thickness. Eight points in the range of 1.50 to 4.00 A/dm² were selected for simulation, combined with the experimental data. The current densities of 2.25, 2.50 and 3.50 A/dm² are validation experiments after simulation. A comparison of the simulated film thickness with the measured film thickness is shown Figure 4.

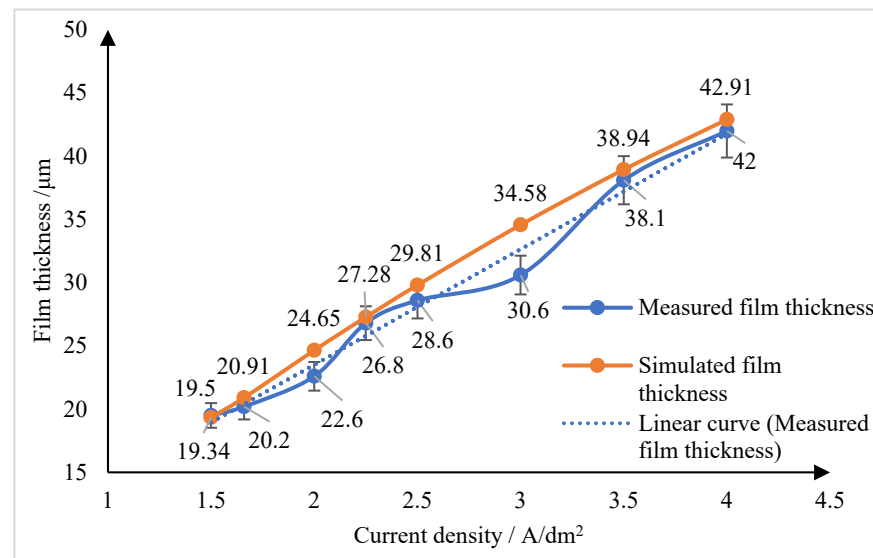


Figure 4. Measured film thickness and simulated film thickness with different current densities (the lines are only guidelines).

It can be found that the overall difference between the simulated film thickness and the experimentally obtained film thickness is small. The largest difference is 3.98 μm at a current density of 3 A/dm² while the other thickness differences are less than 2 μm, which meets the required thickness calculation accuracy. Therefore, it can be concluded that the present model can calculate the anodic oxide film thickness of 6061 aluminum alloy accurately in advance within a certain current density range.

In the constant current mode, oxidation time is directly related to oxide film thickness, which in ideal conditions is proportional to time. In fact, time mainly affects the current efficiency of the anodic oxidation process, and the current efficiency changes in real time with the change of time. This model does not take into account the real-time changes in current efficiency, and the average effect of time on current efficiency is brought into the simulation model to obtain a predictive model related to oxidation time. A comparison of the simulated film thickness with the measured film thickness is shown in Figure 5. The two groups with oxidation times of 75 and 105 min were validation experiments after the simulation.

The maximum difference between the calculated film thickness and the measured film thickness is 3.74 μm when the time is 90 min. The results achieve the required accuracy for film thickness calculations, and it can be assumed that advance calculations of anodic oxide film thickness can be achieved in the range of 20 to 120 min.

Ideally, temperature does not affect oxide film thickness under the premise of constant current. In practice, temperature affects current efficiency during experiments. The effect of temperature on current efficiency is brought into the simulation model to obtain a prediction model for oxide film thickness. Eight points in the range of 10 to 30 °C were selected for simulation calculations, and combined with the experiments, the simulated film thickness and the measured film thickness were obtained as shown in Figure 6. The three groups with temperatures of 18, 22 and 27 °C are validation experiments conducted after simulations.

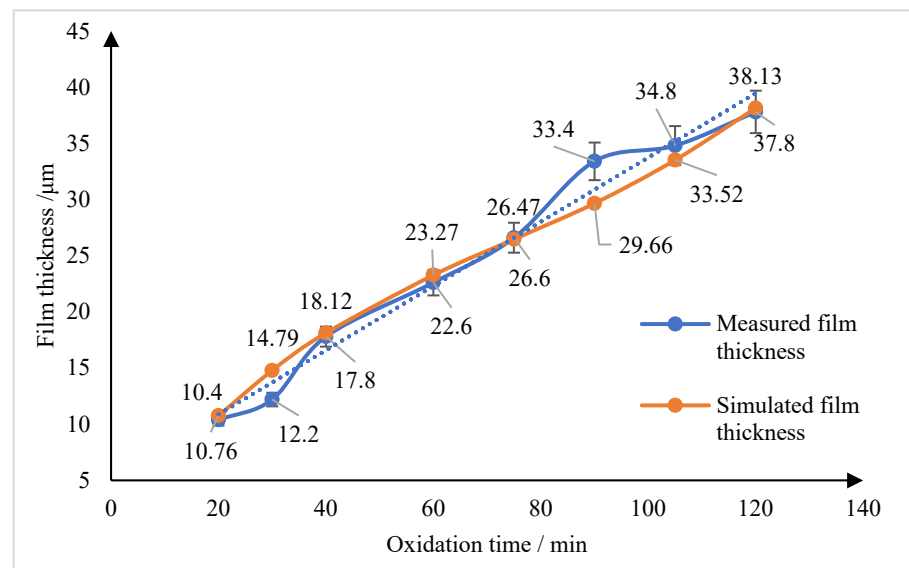


Figure 5. Measured film thickness and simulated film thickness with different oxidation time (the lines are only guidelines).

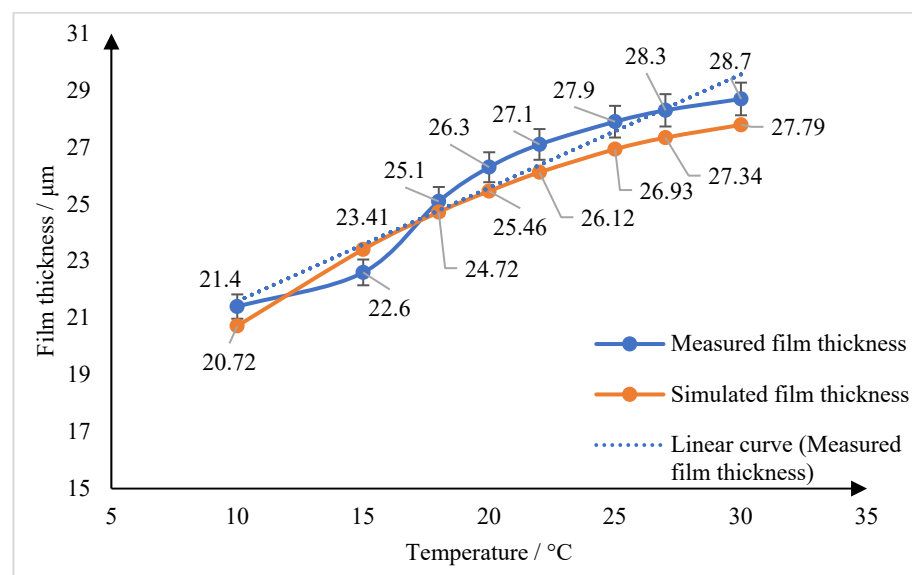


Figure 6. Measured film thickness and simulated film thickness with different temperature (the lines are only guidelines).

The deviations between the simulation results and the actual values of the temperature group are all below $2\ \mu\text{m}$, which meets the requirements for the film thickness calculation accuracy and can be considered as achieving the advance calculation of the film thickness in the range of 10 to $30\ ^{\circ}\text{C}$.

4. Parameter Correlation of Oxide Film Surface Quality and Laser Resistance

The specimens of the current density group (1.5 , 2.0 , 3.0 and $4.0\ \text{A}/\text{dm}^2$), time group (30 , 60 , 90 and $120\ \text{min}$) and temperature group (10 , 15 , 20 and $30\ ^{\circ}\text{C}$) were anodised respectively. After the deposition of CdSe nanoparticles and the sealing process, the specimens were subjected to SEM characterisation and roughness inspection. The SEM characterization of the current density group is shown in Figure 7, and the roughness results are shown in Table 5, where the current density in Figure 7A is $1.5\ \text{A}/\text{dm}^2$, Figure 7B is $2.0\ \text{A}/\text{dm}^2$, Figure 7C is $3.0\ \text{A}/\text{dm}^2$ and Figure 7D is $4.0\ \text{A}/\text{dm}^2$.

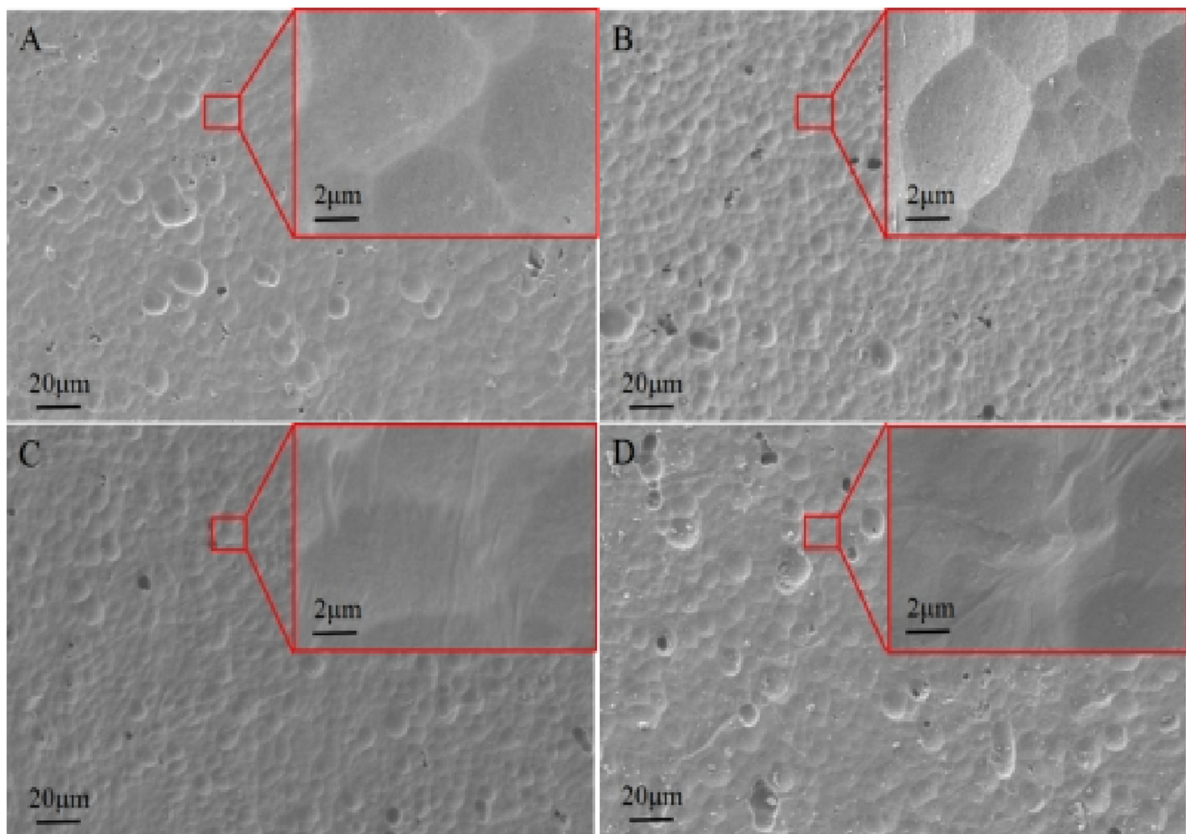


Figure 7. SEM characterization of surface morphology with different current density, (A) is 1.5 A/dm², (B) is 2.0 A/dm², (C) is 3.0 A/dm² and (D) is 4.0 A/dm².

Table 5. Ra and Rmax values with different current densities.

Current Density	Ra	Rmax
1.5 A/dm ²	0.473 μm	5.894 μm
2.0 A/dm ²	0.468 μm	4.265 μm
3.0 A/dm ²	0.626 μm	5.308 μm
4.0 A/dm ²	0.733 μm	6.646 μm

At a current density of 1.5 A/dm² the surface is relatively flat with microscopic pits but with small depths and soft borders. At a current density of 2.0 A/dm² the surface has more microscopic pits and sharp borders with increased depths. When the current density was increased to 3.0 A/dm², stripes appeared inside the microscopic pits. When the current density was increased to 4.0 A/dm², the surface was more broken, the defects increased and stripes also appeared inside the microscopic pits. Overall, when the current density is less than or equal to 3.0 A/dm², the difference in microscopic morphology is small but still tends to deteriorate, which indicates that the sealing process is beneficial to improving the surface morphology of the specimen.

The surface deteriorates significantly when the current density reaches 4.0 A/dm². Ra values increase with increasing oxidation current density, but the difference in Rmax values is small. This is because as the current density increases, the local temperature on the surface of the specimen rises too quickly, accelerating the dissolution of sulphuric acid on the oxide film, so the surface of the specimen is more broken at higher current densities.

The time group SEM characterization is shown in Figure 8, Figure 8A oxidation time is 30 min, Figure 8B is 60 min, Figure 8C is 90 min and Figure 8D is 120 min. The surface roughness of the specimens is shown in Table 6.

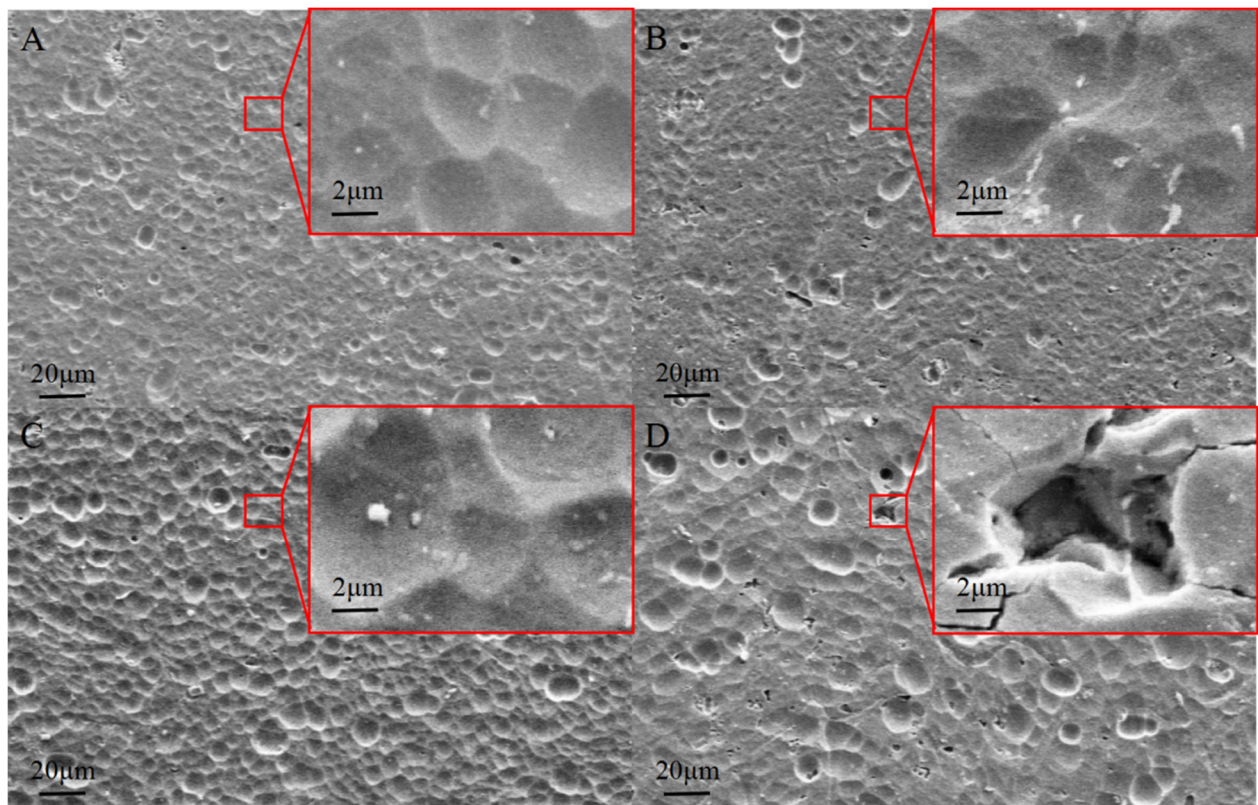


Figure 8. SEM characterization of surface morphology with different current density, (A) is 30 min, (B) is 60 min, (C) is 90 min and (D) is 120 min.

Table 6. Ra and Rmax values with different oxidation time.

Oxidation Time	Ra	Rmax
30 min	0.572 μm	4.858 μm
60 min	0.692 μm	6.529 μm
90 min	0.629 μm	5.713 μm
120 min	0.755 μm	20.475 μm

It is evident that as the oxidation time increases, the teardrop pits on the surface of the oxide film gradually increase and deepen. When the oxidation time is 120 min, deeper defects on the surface of the oxide film have a negative impact on the uniformity of the film. During the roughness test, the Ra value of the oxide film increases with time while the Rmax value only increasing significantly at 120 min. It indicates that the surface quality and roughness of the oxide film increases slightly with time, when the oxidation time does not exceed 90 min. However, when the oxidation time exceeds 120 min, large deep pits appear on the oxide film, which affects the uniformity of the film formation.

The temperature group SEM characterisation is shown in Figure 9, Figure 9A is 10 °C, Figure 9B is 15 °C, Figure 9C is 20 °C and Figure 9D is 30 °C. The surface roughness of the specimens is shown in Table 7.

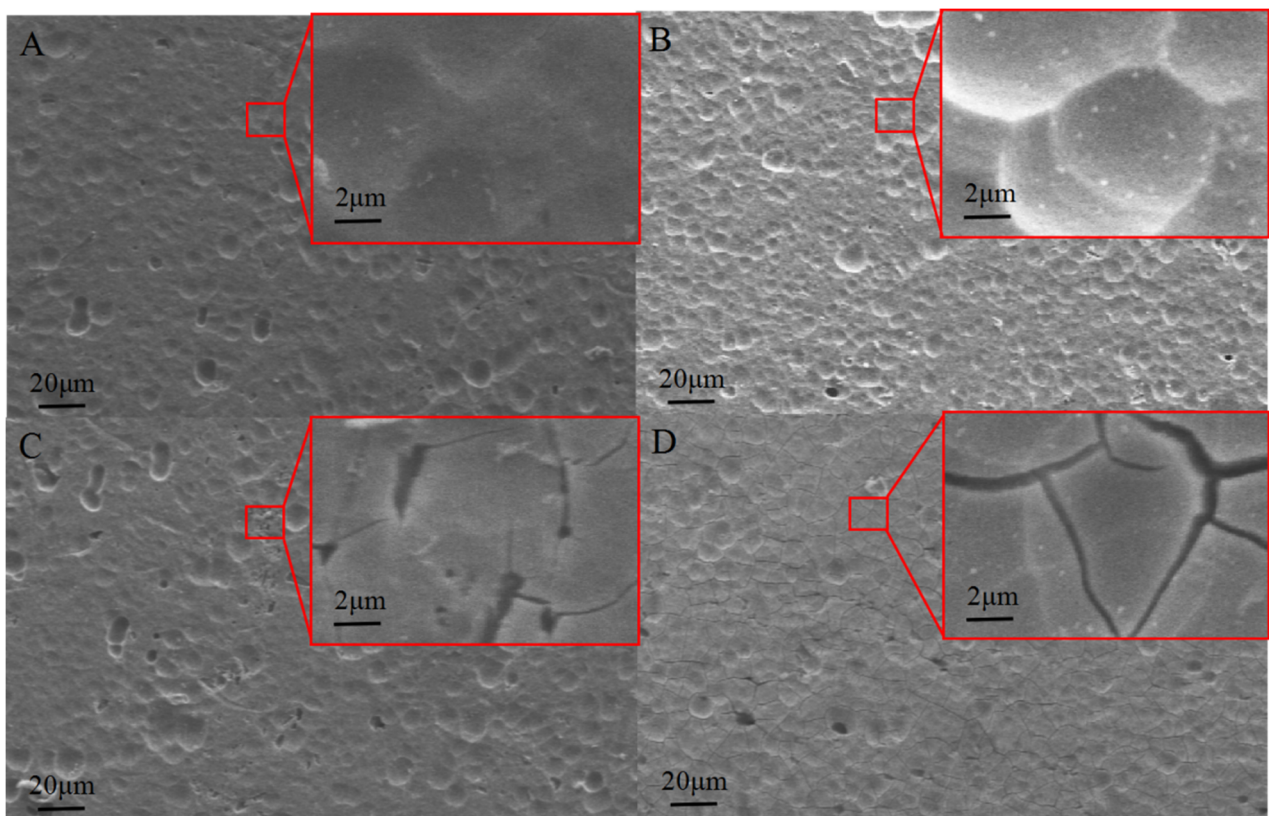


Figure 9. SEM characterization of surface morphology with different temperature, (A) is 10 °C, (B) is 15 °C, (C) is 20 °C and (D) is 30 °C.

Table 7. Ra and Rmax values with different temperature.

Temperature	Ra	Rmax
10 °C	0.696 μm	6.646 μm
15 °C	0.692 μm	6.529 μm
20 °C	0.680 μm	5.290 μm
30 °C	1.058 μm	8.313 μm

Droplet-shaped craters appear on the surface of the specimen at temperatures of 10 and 15 °C, and the difference is that the boundary of the crater is sharper at 15 °C. Tiny cracks begin to appear on the surface when the temperature rose to 20 °C, and the cracks on the surface of the specimens increased significantly as the temperature rose further to 30 °C. It can be assumed that the surface quality of the anodised film deteriorates as the temperature rises. The difference in Ra and Rmax values between the specimens at 10, 15 and 20 °C is not significant, but at 30 °C the Ra and Rmax values increase significantly. The oxide film roughness does not change much in the lower temperature range, but at higher temperatures the oxide film becomes significantly rougher.

The light absorption diagram of the film system in this study is shown in Figure 10. The incident light has a primary reflection on the surface. Because both silicon oxide and pure aluminum oxide are highly transparent materials, the surface reflectivity is extremely low. The light then refracts into the porous aluminum oxide layer and reaches the aluminum alloy substrate at the bottom after being absorbed by the film system. The aluminum alloy is a high reflective material. After the reflection of the substrate and the secondary absorption of the porous layer, the light finally emits out of the film system after the refraction of the surface layer. Here, the refraction between the silicon oxide layer and the porous alumina layer is ignored.

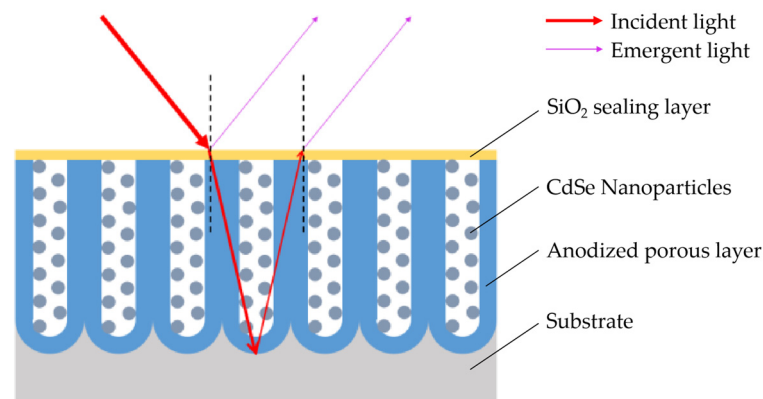


Figure 10. Diagram of light absorption in the film system.

The morphology of the laser damage pits showed two typical characteristics. At thin film layers and high laser energy densities, the film layer underwent brittle fracture and peeled off with a sharp and neat fracture, as shown in Figure 11A. When the laser energy density is low or the film layer is thick, the film layer does not peel off, but becomes a damage pit with a certain slope, the SEM characterization is shown in Figure 11B. This is because when the laser irradiates the light absorbing film, if the laser is completely absorbed by the film and does not reach the substrate, the film will melt under the action of huge energy. The melting position expands, and the upper film layer mechanically collapses along one side to release energy. If the laser reaches the substrate, due to the low melting point of the aluminum alloy, the substrate will melt as a whole, and the upper film will be damaged mechanically. For the interaction between laser and film, please refer to our previous work for details [18].

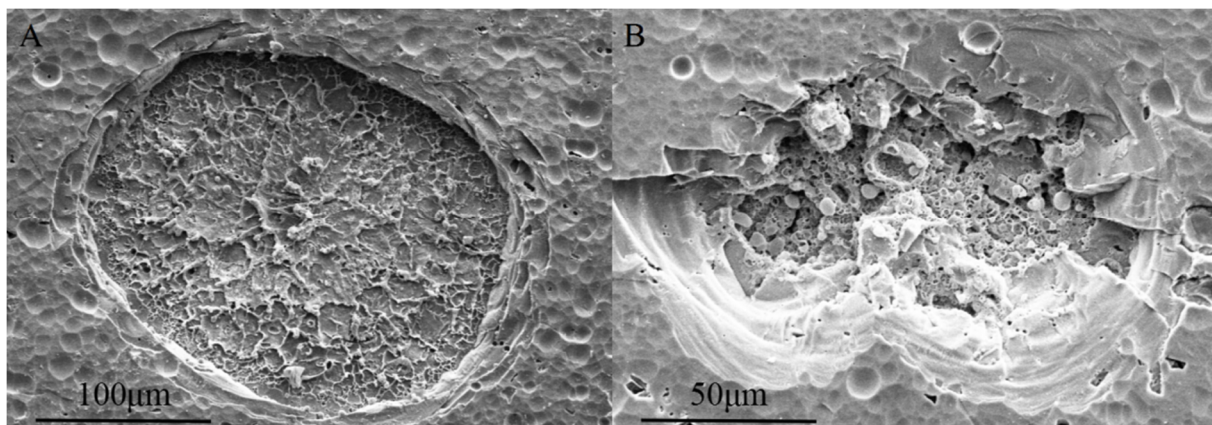


Figure 11. Typical morphology of laser damage pits on anodized films, (A) is complete peeling and (B) is gradient peeling.

The results of the laser damage experiments for current density group are shown below, measuring the relative height of the damage position midpoint as shown in Figure 12. The average damage width, average damage depth and maximum damage depth of different specimens after laser shock at various energy densities are shown in Table 8. When the laser energy density was 0.3 J/cm^2 , the film layer of each group was not damaged. When the laser energy density was 0.5 J/cm^2 , the film layers of the specimens with oxidation current densities of 1.5 and 2.0 A/dm^2 showed damage, and the lower the oxidation current density, the greater the maximum damage depth. When the laser energy density is 1.0 J/cm^2 , all four groups of specimens were damaged, and the lower the oxidation current density, the greater the maximum damage depth. After laser irradiation, the average damage width and the average damage depth are close if no overall peeling of the film layer occurs.

While if overall peeling of the film layer occurs, the average damage width is close to the diameter of the laser spot and the depth is close to the thickness of the film layer. Overall, it appears that the anodising current density and the resistance of the film to laser damage are positively correlated within the scope of this study.

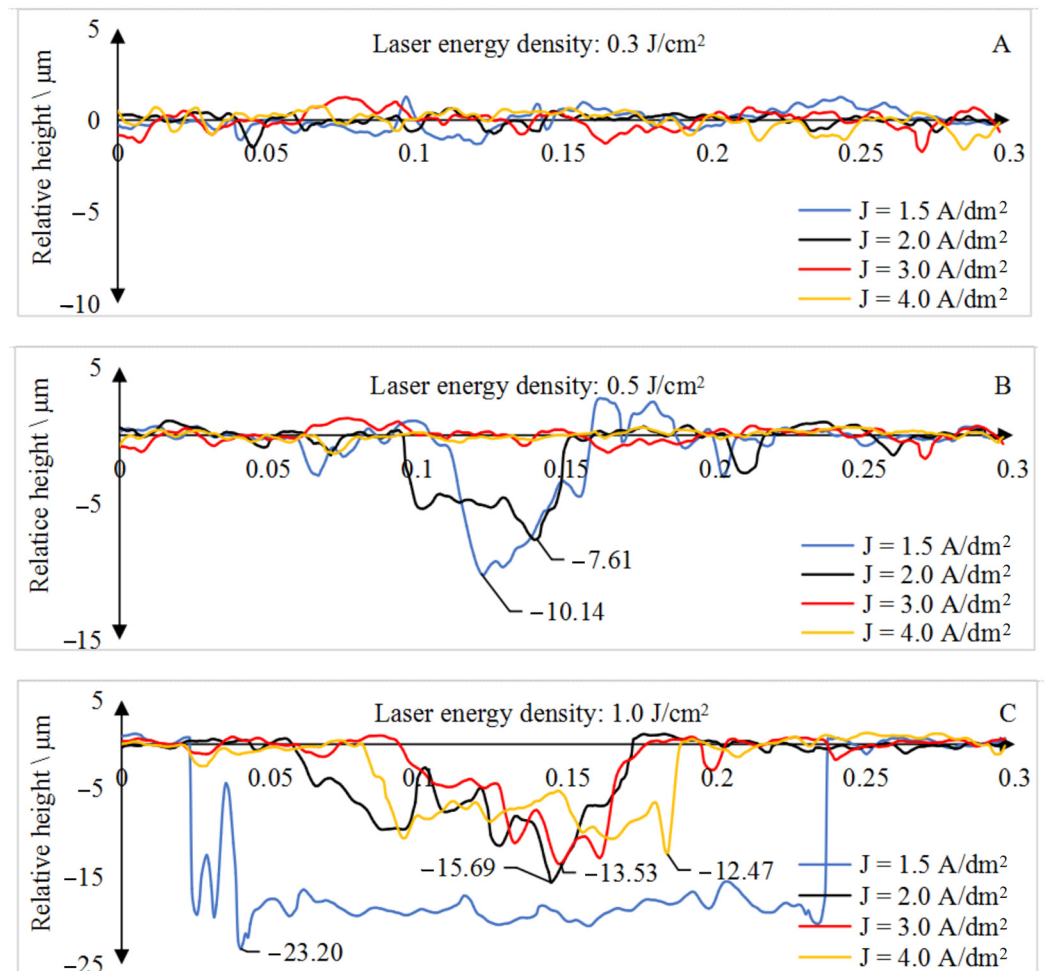


Figure 12. Damage pits profile after laser irradiation with different current densities. The laser energy density in (A) is 0.3 J/cm²; (B) is 0.5 J/cm²; (C) is 1.0 J/cm².

Table 8. Width and depth of laser damage pit of current density group.

Current Density	Energy Density	Average Damage Width	Average Damage Depth	Maximum Damage Depth
1.5 A/dm ²	0.3 J/cm ²	-	-	-
1.5 A/dm ²	0.5 J/cm ²	57 µm	6.64 µm	10.14 µm
1.5 A/dm ²	1.0 J/cm ²	260 µm	18.34 µm	23.20 µm
2.0 A/dm ²	0.3 J/cm ²	-	-	-
2.0 A/dm ²	0.5 J/cm ²	65 µm	5.25 µm	7.61 µm
2.0 A/dm ²	1.0 J/cm ²	137 µm	7.60 µm	15.69 µm
3.0 A/dm ²	0.3 J/cm ²	-	-	-
3.0 A/dm ²	0.5 J/cm ²	-	-	-
3.0 A/dm ²	1.0 J/cm ²	95 µm	7.06 µm	13.53 µm
4.0 A/dm ²	0.3 J/cm ²	-	-	-
4.0 A/dm ²	0.5 J/cm ²	-	-	-
4.0 A/dm ²	1.0 J/cm ²	129 µm	7.78 µm	12.47 µm

The results of the laser damage experiments for the oxidation time group are shown below, measuring the relative height of the damage position midpoint as shown in Figure 13. The average damage width, average damage depth and maximum damage depth are shown in Table 9. When the laser energy density was 0.3 J/cm^2 , the film layer of each group was not damaged. When the laser energy density was 0.5 J/cm^2 , damage occurred in the specimens with oxidation time of 30 min and 60 min, and the specimen with oxidation time of 30 min showed overall peeling of the film layer. When the laser energy density is 1.0 J/cm^2 , all four groups of specimens were damaged, and the specimen with oxidation time of 30 min showed overall peeling. The specimens with oxidation time of 60 min, 90 min and 120 min have similar damage degree. The overall analysis indicates that the resistance of the oxide film to laser damage at lower laser energy densities is positively correlated with the oxidation time. At laser energy densities of 1.0 J/cm^2 , the film layers at lower oxidation times will show overall damage, and the film layers at higher oxidation times show similar damage.

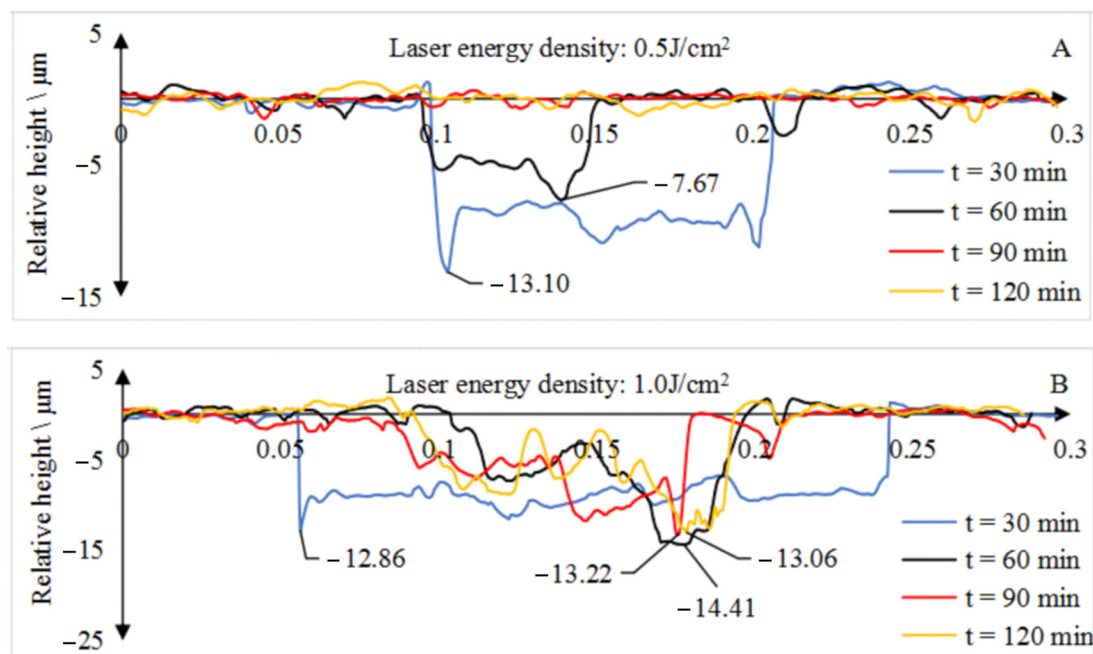


Figure 13. Damage pits profile after laser irradiation with different oxidation time. The laser energy density in (A) is 0.5 J/cm^2 ; (B) is 1.0 J/cm^2 .

Table 9. Width and depth of laser damage pit of oxidation time group.

Oxidation Time	Energy Density	Average Damage Width	Average Damage Depth	Maximum Damage Depth
30 min	0.3 J/cm^2	-	-	-
30 min	0.5 J/cm^2	132 μm	9.02 μm	7.67 μm
30 min	1.0 J/cm^2	227 μm	8.99 μm	12.86 μm
60 min	0.3 J/cm^2	-	-	-
60 min	0.5 J/cm^2	64 μm	5.20 μm	13.10 μm
60 min	1.0 J/cm^2	99 μm	7.69 μm	14.41 μm
90 min	0.3 J/cm^2	-	-	-
90 min	0.5 J/cm^2	-	-	-
90 min	1.0 J/cm^2	110 μm	7.34 μm	13.22 μm
120 min	0.3 J/cm^2	-	-	-
120 min	0.5 J/cm^2	-	-	-
120 min	1.0 J/cm^2	118 μm	6.91 μm	13.06 μm

The relative height of the temperature group are shown in Figure 14. The average damage width, average damage depth and maximum damage depth are shown in Table 10. When the laser energy density was 0.3 J/cm^2 , no damage occurred. When the laser energy density is 0.5 J/cm^2 , the specimens with oxidation temperatures of 15°C , 20°C and 30°C show film damage and the damage depth increases with the increase of laser energy density. When the laser energy density is 1.0 J/cm^2 , all four groups of specimens were damaged. The films of specimens at 10°C and 15°C did not peel off, and the damage depth increased with the increase of temperature. The specimens at 20°C and 30°C have the overall damage of the film, and the depth is close to the thickness of the film. Overall, the anodizing temperature is negatively related to the laser damage resistance of the film.

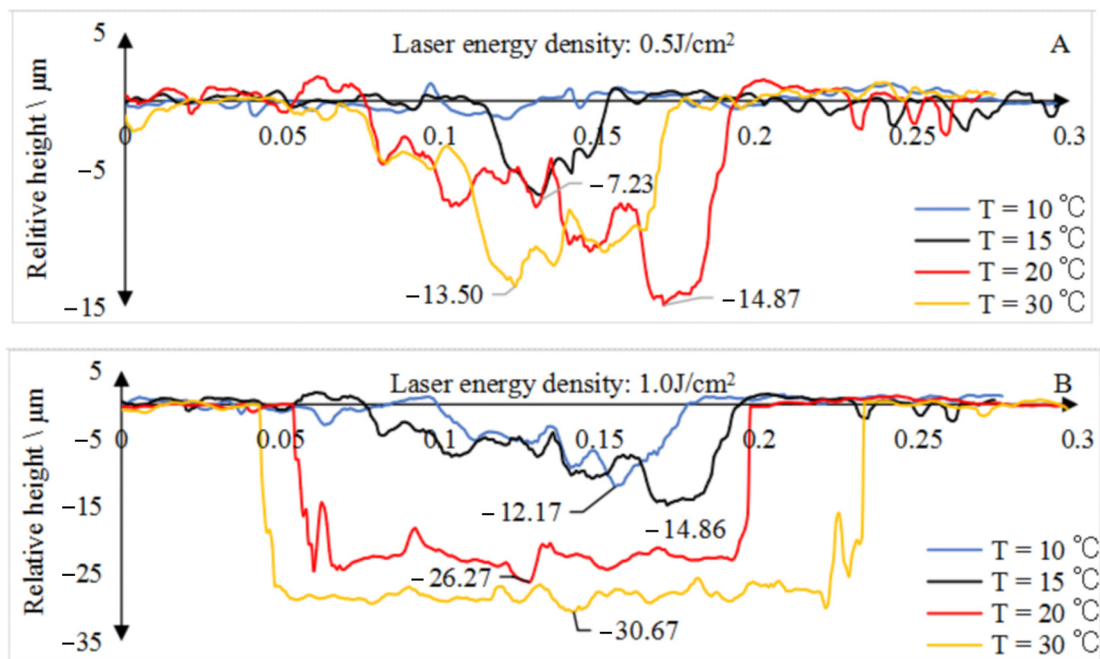


Figure 14. Damage pits profile after laser irradiation with different temperature. The laser energy density in (A) is 0.5 J/cm^2 ; (B) is 1.0 J/cm^2 .

Table 10. Width and depth of laser damage pit of temperature group.

Temperature	Energy Density	Average Damage Width	Average Damage Depth	Maximum Damage Depth
10°C	0.3 J/cm^2	-	-	-
10°C	0.5 J/cm^2	-	-	-
10°C	1.0 J/cm^2	$85 \mu\text{m}$	$6.36 \mu\text{m}$	$12.17 \mu\text{m}$
15°C	0.3 J/cm^2	-	-	-
15°C	0.5 J/cm^2	$41 \mu\text{m}$	$4.13 \mu\text{m}$	$7.23 \mu\text{m}$
15°C	1.0 J/cm^2	$136 \mu\text{m}$	$7.79 \mu\text{m}$	$14.86 \mu\text{m}$
20°C	0.3 J/cm^2	-	-	-
20°C	0.5 J/cm^2	$137 \mu\text{m}$	$7.81 \mu\text{m}$	$14.87 \mu\text{m}$
20°C	1.0 J/cm^2	$174 \mu\text{m}$	$22.13 \mu\text{m}$	$26.27 \mu\text{m}$
30°C	0.3 J/cm^2	-	-	-
30°C	0.5 J/cm^2	$113 \mu\text{m}$	$8.01 \mu\text{m}$	$13.50 \mu\text{m}$
30°C	1.0 J/cm^2	$229 \mu\text{m}$	$27.54 \mu\text{m}$	$30.67 \mu\text{m}$

The reason for the above results is that the thickness of the oxide film increases with the increase of the current density, and the radius of the nanopore also increases. This means that the thickness of the light absorbing layer increases, and the number of CdSe nanoparticles increases. Therefore, the laser damage resistance of the oxide film increases

with the increase of current density. With the increase of oxidation time, the thickness of the oxide film increases, but the overall peeling of the film will still occur within a certain range. However, with the further increase of time, the laser energy is completely absorbed by the light absorbing layer before reaching the substrate, so the film is subject to gradient peeling. Time has little effect on the radius of nanopore, so when gradient peeling occurs, the damage condition is similar. With the increase of temperature, the quality of the oxide film becomes worse, the structure becomes loose and the mechanical strength decreases. Therefore, the laser damage resistance of the oxide film decreases with the increase of temperature.

5. Conclusions

In this paper, the effects of anodizing parameters on the thickness and properties of 6061 aluminum alloy anodized composite films are studied with experiments and simulations, and the thickness calculation model is established. The main research results are summarized as follows:

1. In this certain range of process parameters, the thickness of 6061 aluminum alloy anodic oxide film can be calculated in advance, and the principle of the influence of process parameters on the thickness is analyzed. An oxide film thickness calculation model was established using COMSOL software combined with theoretical calculations, and the deviation of the calculation was within 5%, except for a few cases.
2. In the aspect of surface morphology, with the increase of current density, temperature and oxidation time, the boundary of droplet-like pits on the film surface becomes more sharp and cracks appear. The roughness increases with the increase of current density and time. The laser damage resistance of the film increases with the increase of current density and decreases with the increase of temperature. When the laser energy density is low, the laser damage resistance of the oxide film is positively related to the oxidation time. When the laser energy density reaches 1.0 J/cm^2 , the film with lower oxidation time will be damaged as a whole, while the damage degree of films with higher oxidation time is similar.

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