Corrosion Resistance of Micro/Nano Secondary Structure Al₂₀₃ Film

Hu Wei^{1,2}, Yang Dafeng^{1,2}, Liu Guoquan^{1,2}, Kou Gang^{1,2}, Ma Dongliang^{1,2}, Chen Changbing^{1,2}

¹Research Institute for National Defense Engineering of Academy of Military Science, Luoyang, 471023, China

²Henan Key Laboratory of Special Protective Materials, Luoyang, 471023, China

*Corresponding author e-mail: huwei@nuaa.edu.cn

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Abstract: The most important thing is to build a rough surface and give it low surface energy by surface modification. In this paper, Al2O3 film with different surface morphologies were prepared by three times anodizing under different conditions. The electric field force in the inner layer of the Al2O3 film resulting in the dissolution of pore walls, different shapes of the surface nanobulge are created. electrochemical corrosion resistance, high electrochemical corrosion resistance (impedance value up to $8 \times 107 \ \Omega \cdot \text{cm-2}$, maximum corrosion potential up to -0.42 V) at the time of third-step oxidation of 50 min. This micro-surface structure may be caused by the acid dissolution of porous Al2O3 channels with the help of external electric field, which leads to the etching of pore walls, and the nano-protrusions remaining on the surface are combined into micro-scale clusters, thus forming micro/nano secondary structure.

1. Introduction

Roughness has always been considered to play an important role in surface wettability, and can be used in self-cleaning and anti-fog fields [1]. Many previous studies have done a lot of work on superhydrophobic surface of materials, the most important thing is to build a rough surface and give it low surface energy by surface modification, and based on metal-assisted etching process, vertical pilaster microstructure with micro/nano secondary scale was produced [2, 3]. The structure microfabrication techniques include chemical etching, reactive ion etching, photolithography, anodization, and micro-/nano- machining [4-6]. Although Cortese et al. [7] illustrated a super-hydrophobic surface of the vertical-wallsed micro-pillar arrays with nano-roughness is completely covered, and the super-hydrophobic surface is formed by isotropic plasma treatment with specific etching ions, but the limitation of the traditional method based on the vertical-wallsed micro-pillars is mainly due to the difficulty of manufacturing compatibility between regions of different sizes [8]. Kim et al. [9] put forward a micro-/nano- dual-scale constructured a polymeric surface by using a PTFE replication process and a sandblasted anodic aluminum oxide (AAO) template, the CA of this dual-scale surface was 165°, which is superior to that of the nanosingle-scale surface [10, 11].

In this chapter, Al_2O_3 film with different surface morphologies and roughness were prepared by third time anodizing under the conditions of medium strong acid, low electrolyte temperature and constant direct current, and the difference of corrosion resistance of micro/nano secondary structure Al_2O_3 film with different surface morphologies in 3.5 wt.% NaCl solution was compared by electrochemical technology. It also provides a scientific basis for the development and application of hydrophobic Al_2O_3 film with micro/nano structures with different surface morphologies, further verifies the discussion results of the formation mechanism of Al_2O_3 in the first two chapters, and supplements the existing research results in this field.

2. Experimental

Adopt 5.0 wt.% phosphoric acid solution as electrolyte, pure aluminum foil as anode (thickness 0.4 mm, purity 99.99%), lead plate as cathode, apply 30 mA steady direct current (current density 0.75 A/dm^2) at constant bath temperature of 10 °C, anodize for 3 h, then take it out and wash it with distilled water, and then add phosphorus chromic acid (containing 6.0 wt.% phosphoric acid and 1.8 wt.% chromic acid) The samples after oxidation film removal were washed with distilled water, and then subjected to secondary anodic oxidation for 2 h under the same conditions as the first oxidation. The anodized sample was cleaned and dried, and the third anodization was carried out in constant bath temperature of 5 °C under the same current condition for different oxidation time. Finally, the sample was cleaned and dried with distilled water.

2.1 Test Methods

The surface and composition of upper surface of alumina film observed by JSM-6360LV electron (SEM) and X-ray energy spectrum (EDS penetration depth 3.6 μ m). X-ray diffraction (Philips X' Pert Automatic Diffrac-tometer, Cu Ka) was used for quantitative and phase identification analysis. 0CAH 200 be used to measured the surface CA of alumina film. The electro-chemical workstation (CHI 750C, Chenhua, Shanghai, China) was used to test polarization curves (Tafel) and electro-chemical impedance spectroscopy (EIS) of different specimens (1 cm \times 1 cm), platinum electrode as auxiliary electrode, saturated calomel electrode (SCE) as the reference electrode. Prior to electro-chemical testing, all samples were treated with paraffin and rosin at 1: 1 (mass fraction) for 1 cm² of exposed area. The electrolyte is 3.5 wt.% (mass fraction) NaCl solution, the scanning rate is 2 mV/s, electro-chemical impedance spectra wrere analyzed and fitted with ZSimpWin software.

3. Results and Discussion

3.1 Scanning Electronic Microscopy (Sem) Analysis

Figure 1 shows SEM photos of The surface of anodized alumina has a porous, uniform and multilayer loose honeycomb structure, the holes are communicated with each other, and most of the holes are in an opening state, the average diameter of which may be about 100 nm, there are faults between the hole and the hole. The overlapping porous structure looks like a honeycomb from the front view (Figure 1 (a)). Because of the different depth and fracture of the alumina tubes, a staggered honeycomb structure alumina film is formed in Figure 1 (b).



Fig.1 Sem Images of Honeycomb-Like Alumina Film (a) and Aao Film (B) from Top View under Magnification of 2000.





Fig.2 Sem Images of Oxide Film with Different Time of the Third-Step Oxidation.

Figure 2 is the SEM images of the Al_2O_3 film with different time of the third-step oxidation: 60 min (a), 75 min (b), 90 min (c) and 100 min (d), from the intuitive point of view, as the voltage increases, the porous layers are more loose and the more obvious the stratification of the porous structure in the vertical direction. With the time of third-step anodization more than 30 min, many arched and rounded hills were piled up on the top of porous structure, just like the adhered "debris walls" (b). A large number of needle-like protrusions were combined into clusters to form sharp island-like structure protrusions cover the porous substrate (c). Because of the excessive oxidation, the connection between the hole walls were further eroded and destroyed by electrolyte, and the needle-like structure was oxidized to be finer or even filamentous and agglomerated into small protrusions (d). When the anodization time reaches 60 min, the hole walls were further etched into a "filamentous" structure and generated on the surface of the porous Al_2O_3 film (e).

3.2 Growth Mechanism Analysis



Fig.3 Growth Mechanism of Alumina Film.

The two processes of the formation and dissolution of Al_2O_3 are mutual inhibited, as shown Figure 3. Since the amount of metal dissolved is larger than that of the formed alumina film, with the formation of barrier layers, the volume of alumina film trends to be smaller as the barrier layer is formed, which produces tensile stresses, resulting in cracks. In the final barrier layer on the outer surface, local heating undergoes the cracks to be repaired again, through the formation of micropores and porous layers [12]. As shown in Figure 3, the walls of tube grow longitudinally towards the substrate to form dense channels, the growth is terminated when the walls of tube grow to a certain depth (Figure 3 I). But the generated walls of tube continue to be transversely etched under the action of the electric field (Figure 3 II), the walls of tube gradually became thinner, and left needle-like thin layers remain on the surface of the porous Al_2O_3 made the surface rough (Figure 3 III).

3.3 X-Ray Diffraction (Xrd) Analysis



Fig.4 The X-Ray Diffraction (Xrd) Spectrum of Macroporous Alumina Film.

This roughening of the alumina macroporous structure related in the increase in the crystallinity of the alumina. XRD result do not have a lot of peaks shows that there is not many amorphous alumina exists, the larger peak intensity represents the better crystallinity, a narrow width indicates that the grain size is very small, the increase in alumina crystallinity is conducive to the mechanical hardness and corrosion resistance of alumina holes structure, while small grain is favorable for absorption of microwave, which is consistent with the following experimental results. The standard data for α -alumina in the PDF standard card is substantially the same and for our diffraction pattern showing three alumina reflections ({1014}, {1123}, and {1126}), confirming the presence of α -Al₂O₃ phase (Figure 4). Good crystallinity ensures the stability of the physical and chemical properties of the microstructure of the film, and maintains good surface properties under a certain influence of harsh external conditions.

3.4 Dynamic Potential Polarization Test



Fig.5 Tafel Polarization Plots Obtained for Al₂O₃ Membrane with the Time of Third-Step Oxidation during 20 ~ 60 Min in 3.5 Wt.% Nacl Solution.

Figure 5 shows that the tafel polarization curves of the Al_2O_3 film with the time of third-step oxidation during 20 ~ 60 min, the corrosion current moves negatively (10-10.34 to 10-11.88 A), at the same time, the corrosion resistance of the Al_2O_3 film is potential shifted with the increase in time continuously (-0.68 to -0.452 V). Combined with the CA experimental results above, the roughness of Al_2O_3 film and the solution increases continuously, a solid / liquid hydrophobic barrier strengthen constantly. Therefore, the decrease in corrosion current density values is due to the formation of super-hydrophobic surface structure, the electrolyte is difficult to contact the surface of the samples, which blocked the active sites on the metal surface, and the corrosion resistance of the sample is obviously improved. However, when the time of third-step oxidation reaches 60 min, the excessive oxidation causes serious etching of the walls of Al_2O_3 tube and destroying the original needle-like nanostructure, forming filamentous agglomeration on the surface, reducing the micro-/nano- dual-scale roughness of the Al_2O_3 film, and negatively shifting the corrosion potential of the Al_2O_3 film relative to the needle-like structure, the Al_2O_3 film with a three-step oxidation time of 50 minutes has the best corrosion potential.

3.5 Dynamic Potential Polarization Test





Figure 6 Nyquist plots (a), Bode plot: Z"-lg (frequency) (b) and phase angle-frequency plot (c) of electrochemical impedance spectroscopy for Al_2O_3 membrane samples with the time of third-step oxidation during 20 ~ 60 min in 3.5 wt.% NaCl solution.

Figure 6 (a) shows the Nyquist plots and fitting circuit of samples in 3.5 wt.% NaCl solution, all results have very low relative errors (less than $0.2\% \sim 5\%$), indicated that the settings match well. According to the above experimental results, the surface roughness of the Al_2O_3 film increase continuously with the time of third-step oxidation within $20 \sim 60$ min, and the impedance value increases by 0.5 orders of magnitude in the experimental frequency band with the time of third-step oxidation increases by 10 min. However, when the time of third-step oxidation is 60 min, the oxide film surface became filamentous by over-oxidized, and the micro-/nano- dual-scale roughness of the Al_2O_3 film reduced slightly, so tangential corrosion easily occurs between the solution and the sample, result in the impedance value of the samples decreased slightly. Therefore, the maximum resistance value of the Al₂O₃ film sample is $8 \times 10^7 \ \Omega \cdot cm^{-2}$ when the oxide film surface has needle-like structure, correspond to the time of third-step oxidation of 50 min. In Figure 6 (b), the phase angles of the Al₂O₃ film are increase and widen obviously, which corresponds to the impedance spectrum, indicated that the corrosion resistance were enhanced. Anyway, the phase angles close to 90° in the high frequency region, indicated that the oxide layers are compact and complete. Low impedance and high phase angles in the range of $10^{0} \sim 10^{2}$ Hz, represented the oxide film layer and the internal interaction between the oxide layer and the substrate. As shown in Figure 6 (c), the Z"-lg (frequency) curves of the Al₂O₃ film are very smooth with no obvious fluctuation in slope, indicating that the super-hydrophobic Al_2O_3 film are complete and basically free from defects, and are uniformly corroded rather than point corroded in the corrosion process.

The appropriate equivalent circuit as shown in Figure 6 (a) proposed by González et al. [13, 14], the fitted circuit allows identification of the charge transfer resistor and the solution resistor, which consists of a parallel combination of a charge transfer resistor, a capacitor and a solution resistor, while Rs is the solution resistor. Because of the existence of hydrophobic structure, electrolyte is difficult to permeate, the mass transfer process of electrolyte participating in the interface corrosion reaction may be a slow-moving aggregation, according to Bode diagram, electrolyte permeat into the oxide layer evenly and the interfacial corrosion distribution is uniform, the impedance caused by diffusion process will appear in EIS [15]. CPEp and Rp are the double-layer capacitor and the resistance of charge transfer between the oxide layer and the metal substrate, respectively. CPEb is the capacitance of oxide layer (film layer in non-corrosion inhibition system and corrosion inhibition layer in corrosion inhibition system), Rb is the resistance of pores of oxide film layer, and the capacitance value is easily affected by surface defects, which is simulated by constant phase element, where CPE is determined by coefficient N and component Y0, N represents different physical conditions, such as changes in surface uniformity caused by surface roughness, porous layer formation, corrosion inhibitor adsorption, etc [16]. The capacitance can be calculated by the following formula [17]:

 $C_{\rm dl} = Y_0 (2\pi f_{\rm max})^{n-1}$ (1)

Where, *f* max represents the maximum frequency of the imaginary part of the impedance on the Nyquist diagram.

4. Conclusion

Superhydrophobic Al_2O_3 film with micro/nano secondary coarse structure were prepared by third time anodizing method under the conditions of low temperature, constant DC and phosphoric acid solution, and the changes of surface morphology, surface hydrophobicity and electrochemical corrosion resistance of Al_2O_3 film under different third-step anodizing time were analyzed and compared. It's very important to maintain the temperature of the electrochemical reaction system about 10 ± 0.5 °C and control the current density among $15\sim20$ mA/cm². The change of surface morphology, CA test and EIS test of three kinds of Al_2O_3 film indicate that needle-like Al_2O_3 film has best corrosion resistance ability, corresponding to the time of third-step anodization was 50 min.

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