THE RESEARCH ON PROCESS OF IMPACT FACTORS OF HARD ANODIC OXIDATION FOR 6061 ALUMINUM ALLOY

Wang Jiexiang[1], Zhang Zhengfu[1, 2], Sun Junsai[1*], Huang Shiguo[1], Han Yamei[1], Du Jiang[1, 2]

1. Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming, 650093, P. R. China；
2. Key Laboratory of Unconventional Metallurgy, Ministry of education, Kunming University of Science and Technology, Kunming, 650093, P. R. China；

Keywords： Aluminum alloy; Hard anodic oxidation; Orthogonal test；Room temperature; Corrosion resistance

Abstract

In order to improve the performance of hard anodic oxidation film of the 6061 aluminum alloy，the significantly influential factors were screened by orthogonal test at room temperature. The results showed that the significant factors which contribute to increase the anode oxidation film hardness were as follows: malic acid, lactic acid, current density, sulfosalicylic acid, triethanolamine, sulfuric acid and oxidation time. And with the decreasing of malic acid, lactic acid, current density, sulfosalicylic acid, sulfuric acid and oxidation time, with the increasing of triethanolamine, the hardness of oxide film increased. We can rank these significant factors which are in favor of increasing anode oxidation film corrosion resistance by its effects as follows: current density, oxidation time, sulfosalicylic acid, sulfuric acid, aluminum sulphate and concentration of triethanolamine. Also as the current density, oxidation time and triethanolamine concentration increased, as the sulfosalicylic acid, sulfuric acid, aluminum sulfate concentration decreased, the corrosion resistance of oxide film was improved.

Introduction

Aluminum and aluminum alloy have a variety of anodic oxidation processes，such as sulfuric acid, chromic acid, oxalic acid and phosphoric acid electrolytic oxidation process [1-4]. In recent years, with the development of anodic oxidation and higher request for the performance of the film quality, hard anodic oxidation process developed rapidly. The conventional hard anodic oxidation process uses sulfate electrolyte, under the condition of low temperature and high current density [5-7]. The process condition with large energy consumption, film growth speed is slow, and production cost is high; what is more anodic oxidation under the low temperature, electrolyte temperature would easily exceed its ceiling, which can cause oxide film become loose or other defects such as uneven distribution of oxide film. In addition, taking forced cooling measure can make energy consumption increase, and the control of process parameters is quite harsh requirements, which decrease productivity. So people try not to affect the properties of oxide film in many cases, but improve the hard anodic oxidation temperature, shorten the oxidation time, namely, widen temperature hard anodic oxidation. About the hard anodic oxidation in a wide temperature range, there are many reports both at home and abroad. Common method is that add additive in electrolyte. These additives can make chemical and electrochemical behaviors of anodic oxidation process change, which effectively reduce the bad influence of reaction heat effect in the process of anodizing, and can effectively widen the temperature range of sulfuric acid anodic oxidation in addition don't decrease the thickness and hardness of the oxide film. Yoshio Fukuda [8] added aluminum sulfate and magnesium sulfate in the sulfuric acid electrolyte to study the effects on aluminum alloy anodic oxidation. Shih Hsing - Hsiang [9] studied the performance of the aluminum alloy anodic oxidation film under the action of mixed nitric acid - sulfuric acid, boric acid - sulfuric acid electrolyte and pulse current, and found that oxide film compositions vary with the compositions of electrolyte in the dissolution test of oxide film. T. Takenaka [10] studied the formation of black anodic films on aluminum in acid electrolytes containing titanium complex anion. Shiyong Liu etc. [11] added PTFE particles in the conventional aluminum alloy hard anodic oxidation electrolyte and product the compound hard anodic oxidation film layer containing PTFE particles in 6063 aluminum alloy surface. Jiaju An etc. [12] studied in ZL109 alloy pulse anodic oxidation process under high current density, discussed the influence of sulfuric acid concentration, pulse current density, malic acid, voltage, temperature on the oxide film thickness, thus the optimum technological conditions were determined. Zhelong Yang etc. [13] studied in the effect that added the rare earth additive into during 2A12 aluminum alloy in hard anode oxidation with sulfuric acid - oxalic acid, sulfuric acid - malic acid system on the anodic oxidation process and the properties of hard anodic oxidation film.

In this paper, based on the orthogonal experiment method to screen 6061 aluminum alloy hard anodic oxidation process significantly influential factors in room temperature (18 to 20℃). Select the hardness of aluminum oxide film, corrosion resistant time and film thickness as the evaluation index of the quality of oxide film. Discussed the factors with the selection of sulfuric acid, oxalic acid, malic acid, lactic acid, glycerin, tartaric acid, boric acid, sulfosalicylic acid, triethanol amine, aluminum sulfate, time and current density, and finally confirmed the significant factor that have the impact on quality of oxide film and the trend of factors, made a beneficial exploration to hard anodic oxidation process of 6061 aluminum alloy at room temperature.

Experiment

Sample preparation

The commercial aluminums alloy 6061 were used as test specimens, and the specimens with dimensions 40 mm×50 mm×1 mm were used to grow hard anodic layers. The compositions of alloy are given in Table Ⅰ.

Corresponding author. E-mail address: zhang-zhengfu@163.com

Table Ⅰ Chemical Composition of 6061 Aluminum Alloy (wt. %)

Si	Mg	Cu	Zn	Fe	Mn	Cr	Ti	Al
0.4～0.8	0.8～1.2	0.15～0.4	0.25	0.7	0.15	0.04～0.35	0.15	Bal.

Specimen's pretreatment processes were that: water scrubbing — alkali corrosion (oil removal) —water scrubbing — acid washing (removal oxide film) — water scrubbing.

Hard anodic oxidation process

With a sample that has been dealt before as the anode, lead plate (150 mm × 40 mm × 5 mm) as the cathode, using the DC power supply (DH1720A - 5, Beijing dahua radio factory) in anodic oxidation treatment. The experiment used the low temperature thermostat (Nanjing Xianou Instruments) to control the anodic oxidation temperature, to make the bath solution temperature in 15 ~ 20℃. Anodic oxidation initial current density as 0.5 A/dm^2, gradually increased to the desired current density but divided into 5 ~ 8 times within 30 min and voltage was not controlled, magnetic stirring until the end.

Reagent and drug used in test were analytically pure, specific as follows: sulfuric acid (98 wt%, Chongqing Chuandong), malic acid (Shanghai Xingzhi), glycerin (Guangdong Guanghua Chemical), boric acid (Shanghai Chemical Reagent), aluminum sulfate (Tianjin Chemreagent), oxalic acid, lactic acid, tartaric acid, sulfosalicylic acid and triethanolamine (the above products were provided by the Tianjin Fengchuan Chemical Reagent).

Oxide film test

Visual inspection on Oxide film, the appearance of hard anodic oxidation film should be gray or black, and there should be no defects such as corrosion of the surface traces, burns, obvious mechanical abrasion, dark stripes and oxidation blister.

According to the Chinese national standard GB/T 6462-1986, the thickness of anodic film was tested with an Axiophot type universal metallographic microscope from West Germany. Sample in accordance with the requirements of the metallographic specimen grinding, polishing, then put sample under the universal metallographic microscope, and magnified it 200 times, select ten points on it to measure thickness.

The hardness of anodic film was tested with a HX-1 type microhardness tester from Wuzhong miniature test instrument factory. Test load was 50 g, and loading time was 10 ~ 12 s. Finally tested seven different areas, and averaged after geting rid of the maximum and the minimum.

Refeing to sulfuric acid anodic oxidation film evaluation criteria, we had hard oxide film corrosion experiments, in order to test its corrosion resistance. Components in the solution of drops test were that hydrochloric acid (ρ= 1.19 g/mL, 25 mL), potassium dichromate (3 g), distilled water (75 mL), and solution pH = 1 ~ 2. Drop a drop of solution on the sample surface under test and observed the change of the droplet surface color. Corrosion resistance evaluation standard was the time that the surface of the droplets color changed from orange to green, the longer of the time, and the better of coating corrosion resistance.

Orthogonal experimental design and results

Additive was added into anodizing electrolyte that gave priority sulfuric acid to filter the electrolyte formula of 6061 aluminum alloy hard anodic oxidation process. According to the production experience and the research experiments at both home and abroad, and after many single factor tests, the designed method of hard anodic oxidation of orthogonal test was determined as 12 factors 2 levels (as table Ⅱ, the main factors were screened besides the sulfuric acid concentration, oxidation time, oxidation of current density, and the level of significant factors also were studied), according to the L_{16} (2^{15}) orthogonal table arrangement experiment. In this paper, the hardness of aluminum oxide film, film thickness and the corrosion resistance of membrane as examining index, orthogonal experiment was designed, and the results were shown in table Ⅲ

Table Ⅱ Orthogonal Test Factors and Levels of Aluminum Hard Anodic Oxidation Process

	A	B	C	D	E	F	G	H	I	J	K	L
	sulfuric acid / (g/L)	oxalic acid / (g/L)	aluminum sulfate / (g/L)	malic acid / (g/L)	time / (min)	glycerin / (g/L)	current density / (A/dm^2)	lactic acid / (g/L)	tartar acid / (g/L)	boric acid / (g/L)	triethanol amine / (g/L)	sulfosalicylic acid / (g/L)
1	220	20	8	20	80	20	3.5	20	50	10	40	20
2	100	0	0	0	60	0	2.5	0	0	0	0	0

Table Ⅲ Orthogonal Test Design and Results of Aluminum Hard Anodic Oxidation Process

No.	A	B	C	D	E	F	G	H	I	J	K	L	hardness /(HV)	corrosion resistance / （min）	thickness / （μm）
1	1	1	1	1	1	1	1	1	1	1	1	1	383	40	61.5
2	1	1	1	1	1	1	2	2	2	2	2	2	555	22	48.8
3	1	1	1	2	2	2	1	1	1	2	2	2	446	25	55.6
4	1	1	1	2	2	2	2	2	2	1	1	1	575	15	33.8
5	1	2	2	1	1	2	1	1	2	1	2	2	429	36	66.3
6	1	2	2	1	1	2	2	2	1	2	1	1	474	25	53.8
7	1	2	2	2	2	1	1	1	2	2	1	1	526	25	41.3
8	1	2	2	2	2	1	2	2	1	1	2	2	530	30	37.5
9	2	1	2	1	2	2	1	2	1	1	1	2	540	31	45.6

10	2	1	2	1	2	2	2	1	2	2	2	1	421	27	34.2
11	2	1	2	2	1	1	1	2	1	2	2	1	494	38	67.5
12	2	1	2	2	1	1	2	1	2	1	1	2	521	28	50.6
13	2	2	1	1	2	1	1	2	2	1	2	1	432	24	50
14	2	2	1	1	2	1	2	1	1	2	1	2	486	25	38.8
15	2	2	1	2	1	2	1	2	2	2	1	2	554	50	66.9
16	2	2	1	2	1	2	2	1	1	1	2	1	586	20	51.9

Table IV Analysis of Micro Hardness Range

	A	B	C	D	E	F	G	H	I	J	K	L
k_1	489.750	491.875	502.125	465.000	499.500	490.875	475.500	474.750	492.375	499.500	507.375	486.375
k_2	504.250	502.125	491.875	529.000	494.500	503.125	518.500	519.250	501.625	494.500	486.625	507.625
R	14.500	10.250	10.250	64.000	5.000	12.250	43.000	44.500	9.250	5.000	20.750	21.250

Table V Analysis of Corrosion Resistance Range

	A	B	C	D	E	F	G	H	I	J	K	L
k_1	27.250	28.250	27.625	28.750	32.375	29.000	33.625	28.250	29.250	28.000	29.875	26.750
k_2	30.375	29.375	30.000	28.875	25.250	28.625	24.000	29.375	28.375	29.625	27.750	30.875
R	3.125	1.125	2.375	0.125	7.125	0.375	9.625	1.125	0.875	1.625	2.125	4.125

Table VI Analysis of Thickness Range

	A	B	C	D	E	F	G	H	I	J	K	L
k_1	49.825	49.700	50.913	49.875	58.413	49.500	56.838	50.025	51.525	49.650	49.038	49.250
k_2	50.688	50.813	49.600	50.638	42.100	51.013	43.675	50.488	48.988	50.863	51.475	51.263
R	0.863	1.113	1.313	0.763	16.313	1.513	13.163	0.463	2.537	1.213	2.437	2.013

Results and discussion

The analyses of influential factors of oxide film hardness

In range analysis table, the corresponding parameters of the maximum average k in various factors are the best level. R is the range of the orthogonal experiment, namely the biggest difference among each factor with the different levels of the experimental results, the greater the range, the greater of factor levels affect the result of the experiment. This paper based on the two level orthogonal tables to arrange experiments, and arranged the 12 factors in total. The main purpose was to select several the more important of factors on the influence degree and trend of the evaluation index, because sulfuric acid, oxidation time, current factors are necessary for the experiment, all of these three elements were discussed. In addition, for the rest of the four main influencing factors were discussed.

From table IV, during hard anodic oxidation of the orthogonal experiment, the most significant factors of all the twelve factors in favor of oxide film hardness increase is malic acid concentration, and the influence of boric acid and oxidation time on the oxide film hardness was minimal. According to the influence level the seven significant factors were as follows: malic acid, lactic acid, current density, sulfosalicylic acid, triethanolamine, sulfuric acid and oxidation time. And malic acid concentration of k value maximum k_2 was 529.000; lactic acid concentration of k value maximum k_2 was 519.250; current density of k value maximum k_2 was 518.500; sulfosalicylic acid concentration of k value

maximum k_2 was 507.625; triethanolamine concentration of k value maximum k_1 was 507.375; sulfuric acid concentration of k value maximum k_2 was 504.250; oxidation time of k value maximum k_1 was 499.500. From the results of the orthogonal test, to add additive such as malic acid, lactic acid and sulfosalicylic acid, which components were shown in table 2, oxide film hardness became worse. This suggested that to get better effect, the amount of additives should be reduced appropriately. After adding triethanolamine, the hardness was better than that not to add it and showed the amount of adding triethanolamine on 40 g/L for further screening. For sulfuric acid concentration, the dosage should be about 100 g/L for further screening. But for the current density, too high current density would lead to oxidation film hardness became lower. Presumably due to high current density in the process of oxidation increased calorific value which accelerated the dissolution of the oxide film and reduced the coating hardness. So for the hard anodic oxidation, its current density should be further screening in the vicinity of 2.5 A/dm^2. Oxidation time on oxidation film hardness is minimal impact. The follow-up process could be further screened between 60 ~ 80 min to find the optimal formula. Taking above all into account, we could draw a conclusion that improving the condition of oxidation film hardness during the process, cutting down the concentration of the malic acid, lactic acid, sulfosalicylic acid, sulfuric acid, reducing the current density appropriately, and prolonging oxidation time and increasing the concentration of

triethanolamine, these will be advantageous to improve the hardness of hard oxidation film.

The analyses of influential factors of oxide film corrosion resistance

From table Ⅴ, in hard anodic oxidation of the orthogonal experiment, the most significant factors of all the twelve factors in favor of increasing the oxide film corrosion resistance is current density, but the influence of glycerin concentration on the oxide film corrosion resistance is minimal. According to the influence level, the six significant factors are as follows: current density, oxidation time, sulfosalicylic acid, sulfuric acid, aluminum sulfate and triethanolamine concentration. And current density of k value maximum k_1 was 33.625; oxidation time of k value maximum k_1 was 32.375; sulfosalicylic acid concentration of k value maximum k_2 was 30.875; sulfuric acid concentration of k value maximum k_2 was 30.375; aluminum sulfate concentration of k value maximum k_2 was 30.000; triethanolamine concentration of k value maximum k_1 was 29.875. From the results of the orthogonal test, to add additive of aluminum sulfate and sulfosalicylic acid, which components were shown in table 2 component, oxide film corrosion resistance became worse. This suggested that to get better effect, the amount of additives should be reduced appropriately. After adding triethanolamine the corrosion resistance was better than that not to add it. That shows the amount of adding triethanolamine on 40 g/L for further screening. For sulfuric acid concentration, the dosage should be about 100 g/L for further screening. For the current density, higher current density would improve oxidation film corrosion resistance. So for the hard anodic oxidation, its current density should be further screening in the vicinity of 3.5 A/dm^2. Oxidation time on oxidation film had a greater influence on the corrosion resistance; the follow-up process could be further screened about 80 min to find the optimal formula. Taking above all into account, we could draw a conclusion that improving the condition of oxidation film corrosion resistance during the process, cutting down the concentration of the sulfosalicylic acid, sulfuric acid, aluminum sulfate, enhancing the current density, prolonging oxidation time and increasing the concentration of triethanolamine, these will be advantageous to improve the corrosion resistance of hard oxidation film.

The analyses of influential factors of oxide film thickness

From table Ⅵ, in hard anodic oxidation of the orthogonal experiment, the most significant factors of all the twelve factors in favor of increasing oxide film thickness is oxidation time, and the influence of the concentration of lactic acid on the oxide film thickness was minimal. According to the influence level the seven significant factors were as follows: oxidation time, current density, tartaric acid, triethanolamine, sulfosalicylic acid, glycerin and sulfuric acid concentration. And oxidation time of k value maximum k_1 was 58.413; current density of k value maximum k_1 was 56.838; tartaric acid of k value maximum k_1 was 51.525; triethanolamine concentration of k value maximum k_2 was 51.475; sulfosalicylic acid concentration of k value maximum k_2 was 51.263; glycerin concentration of k value maximum k_2 was 51.013; sulfuric acid concentration of k value maximum k_2 was 50.688. From the results of the orthogonal test, to add additive of triethanolamine, sulfosalicylic acid, glycerin, which components were shown in table 2, oxide film thickness became thinner. This suggested that to get better effect, the amount of additives should

be reduced appropriately. After adding tartaric acid the film thickness is better than that not to add it. That shows the amount of adding tartaric acid on 50 g/L for further screening. For sulfuric acid concentration, the dosage should be about 100 g/L for further screening. For the current density, higher current density would improve oxidation film thickness. This is due to with the generation of the oxide film on the anode; it was electrolyzed again at the same time. Only when the oxide film formation rate was greater than the dissolution rate, oxidation film can smooth growth. Increasing current density would contribute to increasing the generation of oxidation film by the electrochemical reaction rate, thus promoted the thickening of the oxide film. So for the hard anodic oxidation its current density should be further screening in the vicinity of 3.5 A/dm^2. Oxidation time on oxidation film hardness is greatest impact. With the extension of reaction time, the film continued to grow. However, the extension of the time can also lead to defects such as porous membrane layer; the follow-up process can be further screened about 80 min to find the optimal formula. Taking above all into account, we could draw a conclusion that improving the condition of oxidation film thickness during process, cutting down the concentration of the triethanolamine, sulfosalicylic acid, glycerin and sulfuric acid, prolonging oxidation time appropriately, increasing the current density and the concentration of tartaric acid, these would be advantageous to improve the thickness of hard oxidation film.

Conclusions

The seven significant factors which contribute to increasing anode oxidation film hardness are as follows: malic acid, lactic acid, current density, sulfosalicylic acid, triethanolamine, sulfuric acid and oxidation time. With the decreasing of the concentration of malic acid, lactic acid, sulfosalicylic acid, sulfuric acid, the current density, and prolonging oxidation time and increasing the concentration of triethanolamine, it will be advantageous to improve the hardness of hard oxidation film. The six significant factors which are in favor of increasing anode oxidation film corrosion resistance are as follows: current density, oxidation time, sulfosalicylic acid, sulfuric acid, aluminum sulphate and concentration of triethanolamine. And lower the sulfosalicylic acid, sulfuric acid, aluminum sulfate concentration, enhance the current density, prolong oxidation time and increase the concentration of triethanolamine, it will be advantageous to improve the corrosion resistance of hard oxidation film. The seven significant factors which are in favor of increasing anode oxidation film thickness are as follows: oxidation time, current density, tartaric acid, triethanolamine, sulfosalicylic acid, glycerol and sulfuric acid concentration. And cutting down the concentration of the triethanolamine, sulfosalicylic acid, glycerin and sulfuric acid, prolonging oxidation time appropriately, increasing the current density and the concentration of tartaric acid, it will be advantageous to improve the thickness of hard oxidation film.

References

[1] Hui Wang, Hongzhan Yi, Haowei Wang, "Analysis and self-lubricating treatment of porous anodic alumina film formed in a compound solution," *Applied surface science*, 252 (2005), 1662-1667.
[2] FRATILA-APACHINTEI L E, TICHELAAR F D, THOMPSON G E, TERRYN H, SKELDON P, DUSZCZYK J, "A transmission electron microscopy study of hard anodic

oxide layers on AlSi(Cu) alloys," *Electrochimica Acta*, 49(19) (2004), 3169-3177.

[3] MOUTARLIER V, GIGANDET M P, PAGETTI J, "Characterisation of pitting corrosion in sealed anodic films formed in sulphric, sulphuric/molybdate and chromic media," *Applied Surface Science*, 206(1/4) (2003), 237-249.

[4] JAGMINAS A, BIGELIEND D, MIKULSKAS I, "Growth peculiarities of aluminum anodic oxide at high voltages in diluted phosphoric acid," *Journal of Crystal Growth*, 233(3) (2001), 591~598.

[5] Xiao-wei WEI, Chao-yin CHEN, "Influence of oxidation heat on hard anodic film of aluminum alloy," *Trans. Nonferrous Met. Soc. China*, 22(2012), 2707−2712.

[6] Lee W, JI R, Gösele U, et al., "Fast fabrication of long-range ordered porous alumina membranes by hard anodization," *Nature Materials*, 5(2006), 741-746.

[7] Rajendra A, Parmar B J, Sharma A K, et al., "Hard anodization of aluminum and its application to sensorics," *Surface Engineering*, 21(3) (2005), 193-197.

[8] Yoshio Fukuda, Toshiro Fukushima, "Anodic oxidation of aluminum in sulphuric acid containing aluminum sulphate or magnesium sulphate," *Electrochimica Acta*, 28 (1) (1983), 47-56.

[9] SHIH H H, TZOU S L, "Study of anodic oxidation of aluminum in mixed acid using a pulsed current," *Surface and Coating Technology*, 124(2) (2000), 278~285.

[10] TAKENAKA T, HABAZAKI H, KONNO H, "Formation of black anodic films on aluminum in acid electrolytes containing titanium complex anion," *Surface and Coatings Technology*, 169/170(2) (2003), 155~159.

[11] Liu Shiyong, Zhang Huichen，Gao Xuemei, et al., "Study of composite hardcoat anodizing of aluminum alloy 6063 and its friction behaviors," *TRANSCTIONS OF MATERIALS AND HEAT TREATMENT*, 5 (2004), 1146-1148.

[12] AN Jiaju, WEI Xiaowei, "Study of a rapid hard anodizing process for aluminum alloy under high currents," *ELECTROPLATING & FINISHING*, 6(2005), 29-31.

[13] Yang Zhelong, Fang Haitao, An Maozhong, et al., "Effert of Rare-earth Additives on Hard Anodizing of Aluminum Alloy," *Material Engineering*, 7(1998), 6-8.