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ARTICLE

Effects of Current Densities on ZL108 Aluminum Alloy MAO Coatings in Electrolyte Containing Graphite Micro-particles

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Abstract: Micro-arc oxidation (MAO) coatings were prepared on ZL108 aluminum alloy in the Na_2SiO_3 electrolyte containing graphite micro-particles at different current densities (1, 5, 10, 15 and 20 A/dm^2). The characteristics of MAO coatings were studied by SEM, EDS, XRD, eddy-current thickness meter and micro-hardness tester. The results show that the thickening of MAO coatings leads to an increase in the oxidation voltages with the increase of current density. The surface of the MAO coatings appears to be porous. The diameter of micropores and the size of sintering discs gradually increase. The relative contents of C and Si elements on the surface of MAO coatings increase with increasing the current density. The C element is uniformly distributed on the surface of MAO coatings. The C element in the cross-section of MAO coatings is mainly concentrated on outer side. MAO coatings mainly consist of SiC, SiO_2, θ-Al_2O_3 and α-Al_2O_3. The SiC phase is derived from the reaction of SiO_2 with graphite. With the increase of current density, the MAO coating hardness increases. MAO coatings prepared at 5 A/dm^2 exhibit the lowest corrosion rate.

Key words: micro-arc oxidation; ZL108 aluminum alloy; current density; graphite; characteristic

ZL108 is a kind of important aluminum-silicon alloy with low-density, high strength, low-thermal expansion coefficient, good heat resistance and excellent casting performance. At present, it has been widely used in the manufacture of various types of engine piston[1,2]. However, ZL108 aluminum alloy exhibits lower surface hardness and poor corrosion resistance, which affects its application ranges and life-span[3]. A series of surface modifying engineering techniques, such as electroplate, plasma spraying and anodic oxidation, have been developed to improve the surface property of aluminum-silicon alloys. However, the present electroplating solution mainly contains heavy metal ions [4], which can inevitably cause pollution. Plasma sprayed coating is mainly mechanically bonded to the substrate [5], which results in the low bonding strength between coating and substrate. The coating produced by anodic oxidation is thinner with lower hardness on aluminum-silicon alloys [6]. Micro-arc oxidation (MAO), an effective and environment-friendly surface treatment technique compared with those techniques can in-situ form ceramic coatings on the surface of valve metals such as Al, Mg, Ti and their alloys [7]. The high hardness and good corrosion resistance of MAO coatings [8,9] can greatly improve surface properties of valve metals and their alloys. The properties of MAO coatings are determined by multi-factors, including current density [10,11], additive [12,13] and electrolyte [14,15]. It has been proved that adding graphite micro-particles to the electrolyte [16,17] provides good wear resistance and corrosion resistance for aluminum alloys compared with the MAO coatings without adding graphite micro-particles. Therefore, it is a viable option that to add graphite in electrolyte in order to improve the surface properties of MAO coatings. However, MAO coatings with excellent properties can be produced with suitable collocation of parameters. The current density has a great influence on micro-hardness, thickness, corrosion resistance, surface morphology and element distribution. Hence, it is very necessary to study the influence of current density on the characteristics of MAO coatings on ZL108 aluminum alloy in an electrolyte containing graphite micro-particles.

In this work, MAO coatings were prepared on ZL108

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aluminum alloy by varying current densities (1, 5, 10, 15, 20 A/dm^2) in the solution of the Na_2SiO_3 electrolyte with added 6 g/L graphite micro-particles. The change in oxidation voltage with time at different current densities was recorded. The micro-hardness, thickness, surface morphology, element content, phase composition and corrosion resistance of MAO coatings were characterized. The characterization of MAO coatings was discussed.

1 Experiment

The size of ZL108 aluminum alloy sample was 5 mm×5 mm×5 mm. The nominal composition (wt%) of this alloy was: 11~13 Si, 1~2 Cu, 0.4~1 Mg, 0.3~0.9 Mn, 0.7 Fe and the balance Al. The samples were polished with abrasive paper and degreased in hot-water at 90 °C before MAO treatment.

The main electrolyte was a solution containing 15 g/L Na_2SiO_3, 0.1 g/L NaOH and 3 mL/L $C_3H_8O_3$. In addition, 6 g/L graphite micro-powder with a size about 30 μm was added to the electrolyte as an additive. During the MAO treatment, the electrolyte temperature was controlled lower than 30 °C by cooling systems of the MAO machine. A direct current power was applied. Current density was fixed at 1, 5, 10, 15 and 20 A/dm^2. The treatment time was 30 min. After the treatment, the samples were sealed in hot-water at 90 °C and dried in air.

The voltage-time curve was recorded by a computer of the MAO machine (WDL 20-6). The morphologies and element contents of surface and cross-section of MAO coatings were investigated by scanning electron microscope (SEM, ZEISSEVO MA15) and energy dispersive spectrometer (EDS, OXFORD 20). The micro-hardness of MAO coatings was characterized by a micro-hardness tester (HXD-2000TM/LCD) with Vickers indenter at a load of 100 g, and the thickness was evaluated by eddy-current thickness meter (TT230). The crystallographic characteristics of MAO coatings were investigated by X-ray diffraction (XRD, DX-2700B). The potentiodynamic polarization curve was used to evaluate the corrosion resistance of MAO coatings by an electro-chemical workstation (Autolab PGSTAT302N). ZETA potential meter (Zetaprobe) was applied to analyze the surface charge of graphite in electrolytes.

2 Results and Discussion

Fig.1 shows the variation of oxidation voltage with time at different current densities (1, 5, 10, 15, 20 A/dm^2). It can be observed that the oxidation voltage increases first, and then gradually stabilizes with the time. The terminal voltages increase with the increase of current densities. The terminal voltages at the current densities of 1, 5, 10, 15 and 20 A/dm^2 are 350, 439, 524, 556 and 587 V, respectively. In fact, the oxidation voltage was positively associated with the resistance of the MAO coatings. As the higher current density can accelerate the growth of the coatings, the thicker coatings can be formed at the same time. The thickness of MAO coatings increased (Fig.2) and led to the increase in the resistance of the MAO coatings. Hence, the terminal voltages increased with the increase of current densities.

The SEM surface morphologies of the MAO coatings at different current densities are shown in Fig.3. At relatively lower current density, the MAO coatings exhibit a uniform surface with micro-pores. With the increase of current density, the diameter of the micro-pores increases and the size of the sintering discs enlarges on the surface of coatings. It has been reported that the micro-pores are discharge channels and the diameter of micro-pore is related to the discharge intensity[18]. The high voltage produced by the high current density caused the strengthened discharge. A part of MAO coatings was melted at the high temperature during discharge. The melts formed sintering discs by cooling the electrolyte. Hence, the stronger discharge caused more melts to form larger sintering discs. At the same time, larger diameter micro-pores were formed by the stronger discharge. As a result, the surface roughness of the MAO coatings increased with the increase of current density.

The EDS spectra of the surface of MAO coatings at different current densities are presented in Fig.4. It is shown that the relative counts of C, Si and O elements increase with the increase of current density. However, the relative counts

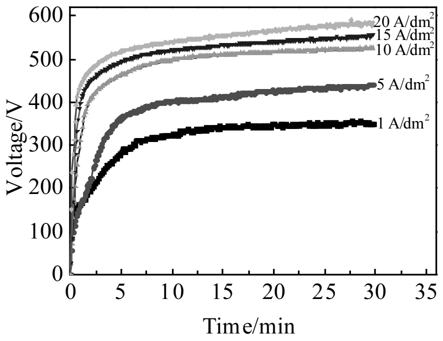

Fig.1 Variation of oxidation voltage with time at different current densities

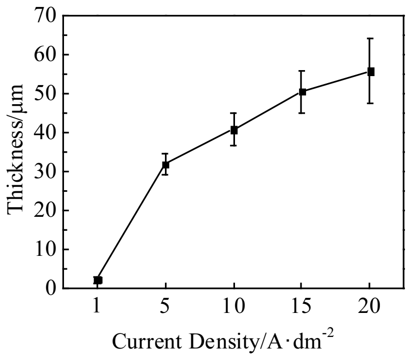

Fig.2 Thickness of MAO coatings at different current densities

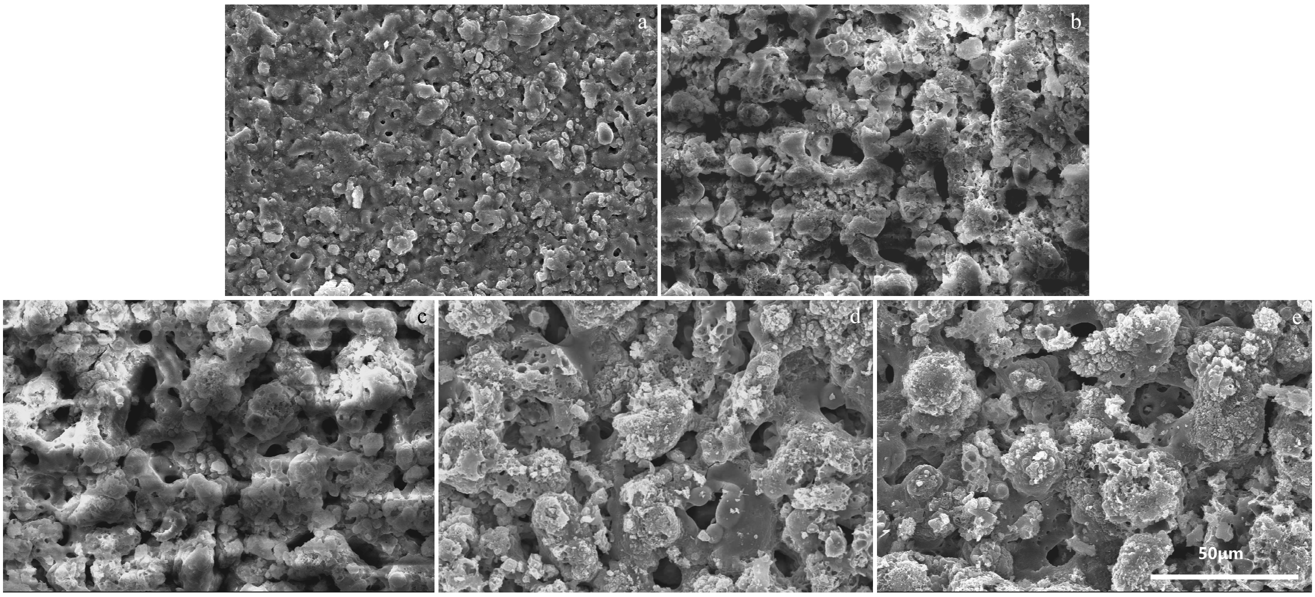

Fig.3 SEM images of MAO coatings at different current densities: (a) 1 A/dm^2, (b) 5 A/dm^2, (c) 10 A/dm^2, (d) 15 A/dm^2, and (e) 20 A/dm^2

of Al element decrease. Under the electric field, the SiO_3^{2-} particles with negative charge will move to the anode and generate SiO_2 during discharge [19]. The increase of current density led to the increase of the electric field strength, which promoted the migration rate of SiO_3^{2-}. The stronger discharge also promoted the transformation from SiO_3^{2-} to SiO_2. Additionally, the extent of the chemical reaction of Si in the substrate reacting with O_2 to generate SiO_2 was also increased with the increase of current density. The surface charge of graphite micro-particles in electrolytes is −63.2 mV by the Zeta potential instrument. Thus, graphite micro-particles would migrate on the surface of MAO ceramic coating by electrophoresis. However the size of graphite micro-particles was around 30 μm and it was difficult for graphite micro-particles to be involved in MAO coatings from the discharge channels. Studies have shown that the graphite reacts with oxygen to form CO and CO_2 at high temperatures (>500 °C), and the higher the temperature, the more serious the reaction [20]. The reaction of graphite micro-particles with oxygen decreases the size of graphite micro-particles, ensuring that the graphite micro-particles enter the micro-pores and take part in the chemical and electrochemical reactions. The reaction of graphite and oxygen is as follows [20]:

$$\text{C (graphite)} + O_2 \xrightarrow{500\,^{\circ}\text{C}} CO_2 \tag{1}$$

$$\text{2C (graphite)} + O_2 \xrightarrow{500\,^{\circ}\text{C}} 2CO \tag{2}$$

As the discussion of above, the relative counts of C and Si increased on the surface of MAO coatings with the increase of current densities, while the relative mounts of Al decreased.

The distribution of C element on the surface of MAO coatings at different current densities is shown in Fig.5. Although the distribution of the C element is relatively uniform, the C element at a higher current density is denser on the surface of MAO coatings. As the discussion of graphite oxidation above, the higher current density led to the greater oxidation rate of graphite. The more and smaller graphite micro-particles entered the micro-pores and took part in the reactions, which caused the C element to gradually become dense and uniformly distributed on the surface of coatings.

The SEM images and C element distribution on cross-section of MAO coatings are represented in Fig.6 and Fig.7. It can be observed that the thickness of MAO coatings apparently increases due to the increasing input current density.

In addition, the results of EDS line scanning show that the C element is mainly concentrated on the outer side, which

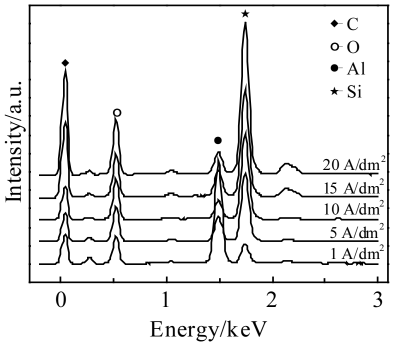

Fig.4 EDS spectra of MAO coatings at different current densities

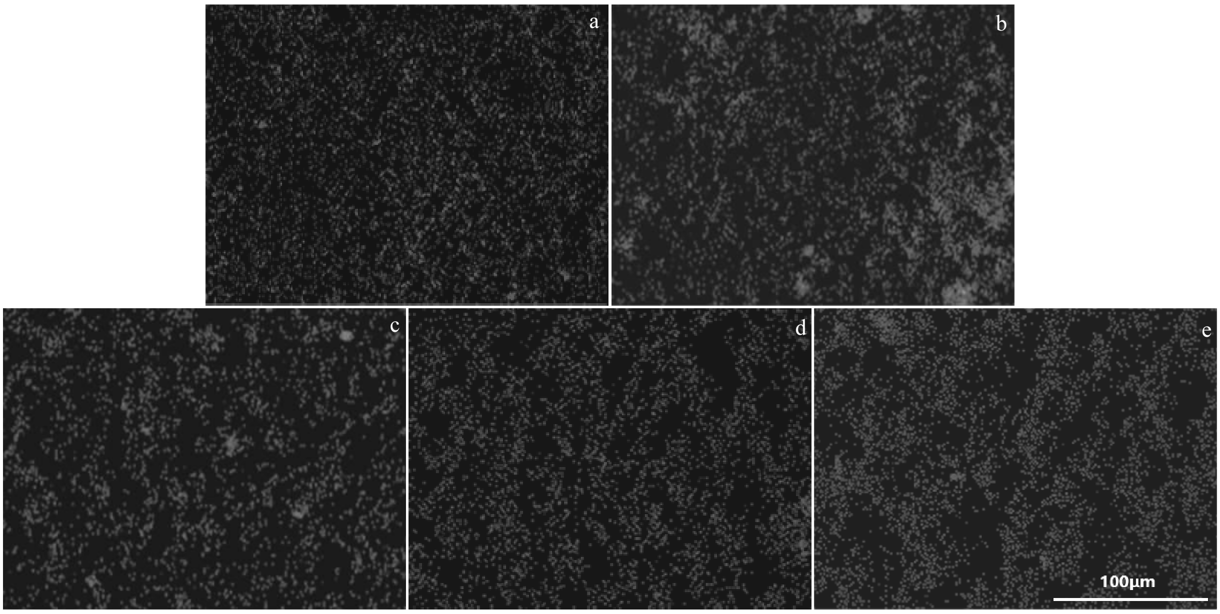

Fig.5 Distribution of C element on the surface of MAO coatings at different current densities: (a) 1 A/dm^2, (b) 5 A/dm^2, (c) 10 A/dm^2, (d) 15 A/dm^2, and (e) 20 A/dm^2

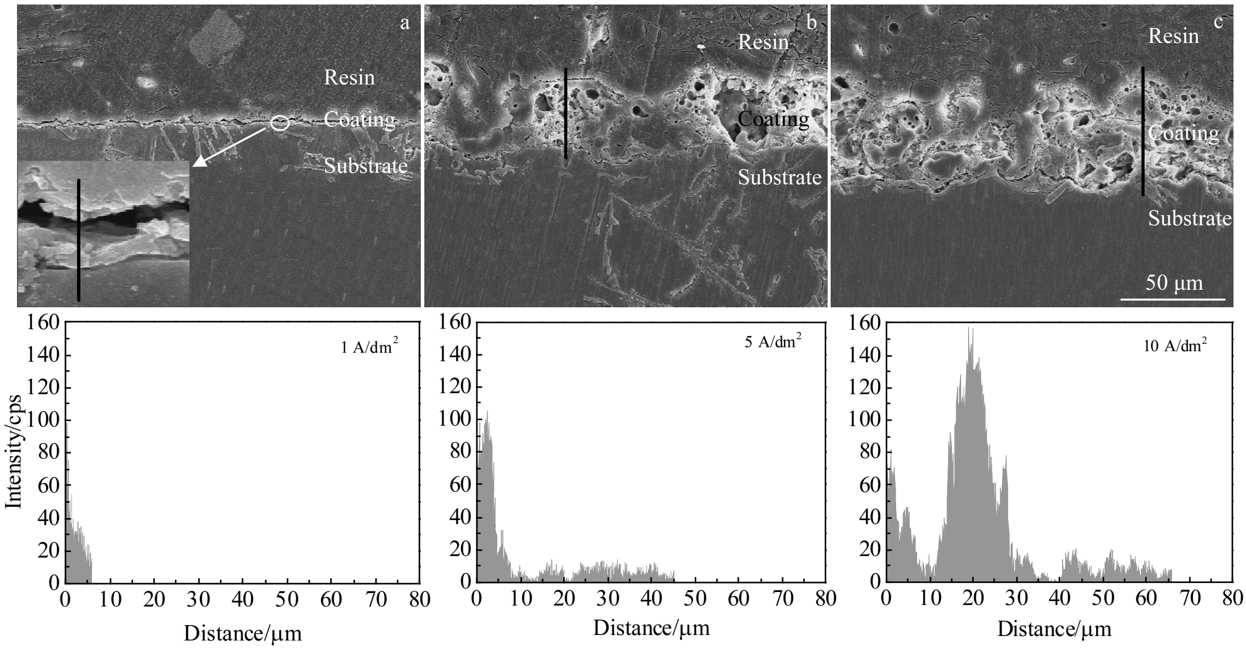

Fig.6 SEM images and C element distribution on cross-section of MAO coatings at different current densities: (a) 1 A/dm^2, (b) 5 A/dm^2, and (c) 10 A/dm^2

reveals that C comes from the electrolyte and enters the coatings during the MAO process. With the increase of current density, the C element shows an increasing trend on outer side. It may be explained that the larger pore on the surface of coating at higher current density is favorable for graphite to enter the coating.

Fig.8 shows the micro-hardness of MAO coatings at different current densities. The average micro-hardness is 1359.8, 1547.2, 1613.3, 1708.6, 2071.3 MPa at different current densities of 1, 5, 10, 15, 20 A/dm^2, respectively. The EDS results show that the relative counts of C and Si on the surface of MAO coatings change regularly in accordance

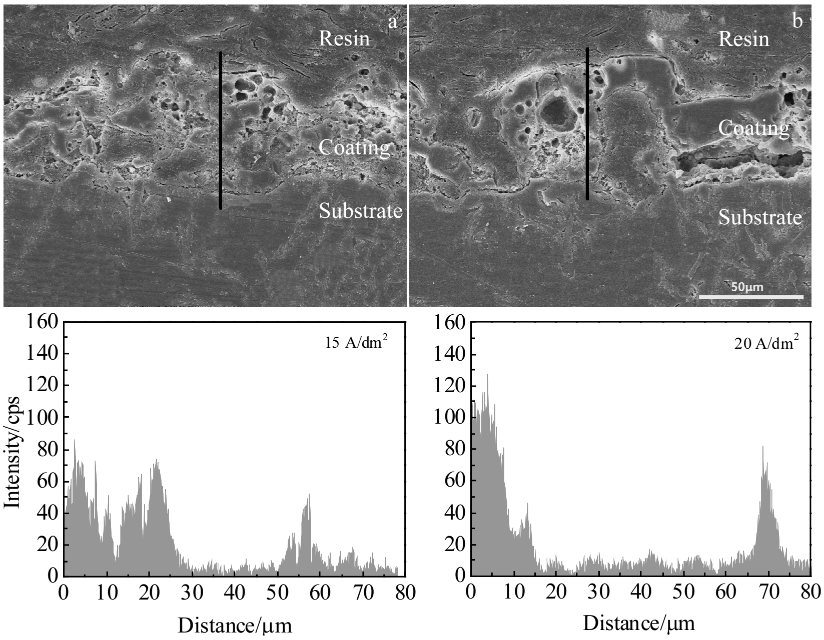

Fig.7 SEM images and C element distribution on cross-section of MAO coatings at different current densities: (a) 15 A /dm^2 and (b) 20 A /dm^2

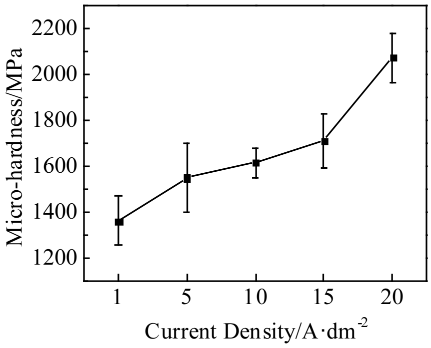

Fig.8 Micro-hardness of MAO coatings at different current densities

with the rising of current densities. Meanwhile, it was found that by XRD that the C and Si exist as SiC and SiO_2 in the MAO coatings. Hence, the increase of thickness of coatings and the contents of hard-phases on the surface of coatings together contribute to the increased micro-hardness of MAO coatings with increasing the current density.

Fig.9 exhibits the XRD patterns of MAO coatings at different current densities. It is clear from these data that MAO coatings mainly consist of SiC, SiO_2, θ-Al_2O_3 and α-Al_2O_3. The Si and Al phases are mainly derived from the substrate. The θ-Al_2O_3, γ-Al_2O_3 and α-Al_2O_3 phases were transformed by amorphous Al_2O_3 in the discharge [21]. In addition, SiC phase was found in MAO coatings. Related literatures have synthesized SiC by the reaction of graphite with SiO_2 [22]. Reaction of graphite with SiO_2 is as follows [22]:

$$SiO_2 + 3C\ (\text{graphite}) \rightarrow SiC + 2CO \tag{3}$$

The reaction heat of the above reaction can be calculated as follows:

$$\begin{aligned}\Delta H_m^{\Theta}(298.15\ \text{K}) &= [2\Delta_f H_m(\text{CO, g, } 298.15\ \text{K}) + \Delta_f H_m(\text{SiC, s, } 298.15\ \text{K})] + [(-1)\ \Delta_f H_m(\text{SiO}_2\text{, s, } 298.15\ \text{K}) + (-3)\Delta_f H_m(\text{C, s, } 298.15\ \text{K})] \\ &= 624.34\ \text{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S_m^{\Theta}(298.15\ \text{K}) &= [2\Delta_f S_m(\text{CO, g, } 298.15\ \text{K}) + \Delta_f S_m(\text{SiC, s, } 298.15\ \text{K})] + [(-1)\ \Delta_f S_m(\text{SiO}_2\text{, s, } 298.15\ \text{K}) + (-3)\ \Delta_f S_m(\text{C, s, } 298.15\ \text{K})] \\ &= 353.25\ \text{J/(K·mol)}\end{aligned}$$

$$\begin{aligned}\Delta G_m^{\Theta}(298.15\ \text{K}) &= \Delta H_m^{\Theta}(298.15\ \text{K}) - T\Delta S_m^{\Theta}(298.15\ \text{K}) \\ &= 624.34\times10^3 - 353.25T\end{aligned}$$

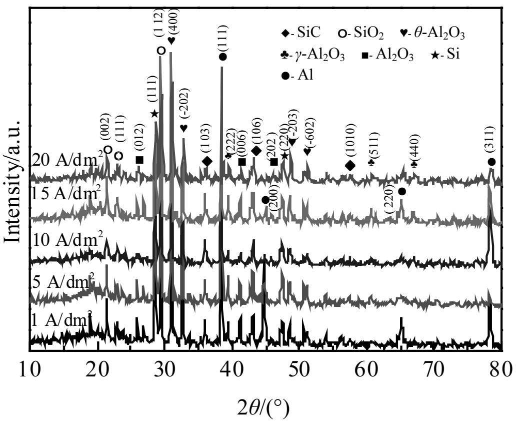

Fig.9 XRD patterns of MAO coatings at different current densities

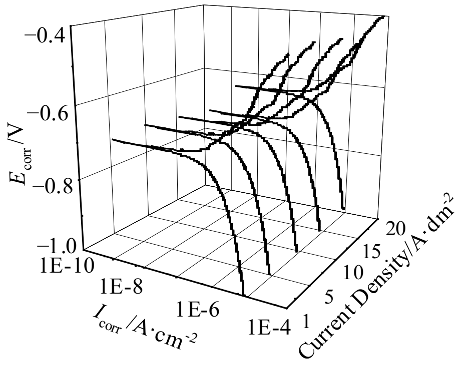

Fig.10 Potentiodynamic polarization curves of MAO coatings at different current densities

Table 1 Fitted corrosion rates of the polarization curves of MAO coatings

i/A·dm^{-2}	i_{corr}/×10^{-6}A·cm^{-2}	E_{corr}/V	V_{corr}/mm·a^{-1}
1	2.4309	−0.69077	0.21926
5	1.5821	−0.65608	0.14269
10	9.1005	−0.69205	0.82083
15	6.0503	−0.66803	0.54571
20	9.6184	−0.66949	0.86754

Obviously, when the temperature was above 1767.417 K, ΔG_m^Θ(298.15 K) < 0, indicating that this reaction can occur spontaneously. During the micro-arc oxidation process, the temperature of discharge zone exceeds 2000 K in a short time[23]. It is obvious that graphite can easily react with SiO_2 to form SiC during the micro-arc oxidation process.

Fig.10 shows the polarization curves of MAO coatings in 3.5wt% NaCl solution at different current densities. The fitted corrosion rates of the curves are 0.21926, 0.14269, 0.82083, 0.54571 and 0.86754 mm/a, as shown in Table 1.

The thicker coating was propitious to obstruct the transfer of the Cl^- during the corrosion process. Hence, the corrosion rate was decreased as the thickness of MAO coatings increased from 1 A/dm^2 to 5 A/dm^2. Meanwhile, the diameter of the micro-pores also increased obviously with the increase of thickness of the MAO coatings. The Cl^- can easily reach the substrate through the micro-pores with large diameter. Then, the corrosion rate increased from 10 A/dm^2 to 20 A/dm^2.

3 Conclusions

1) MAO coatings are prepared on ZL108 aluminum alloy at different current densities in a silicate electrolyte containing graphite micro-particles.

2) With the increase of current density, the growth of the coatings is accelerated, which leads to an increase in the thickness, and then the oxidation voltage and micro-hardness increase.

3) The diameter of the micro-pores increases and the size of the sintering discs enlarges on the surface of coatings with the increase of current densities. The relative contents of C and Si gradually increase on the surface of coatings. The C element is mainly concentrated on the outer side on cross-section of MAO coatings. The coating mainly consists of SiC, SiO_2, θ-Al_2O_3 and α-Al_2O_3. The corrosion rate shows a trend to decrease first and then increase due to the combined effects of the thickness of the coatings and diameter of the micro-pores.

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含石墨微粒电解液电流密度对ZL108微弧氧化膜层特性的影响

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摘　要：在含石墨微粒的硅酸钠电解液中，采用不同的电流密度（1, 5, 10，15和20 A/dm^2）在ZL108铝合金上制备了微弧氧化（MAO）膜层。利用SEM、EDS、XRD、涡流测厚仪和显微硬度计对微弧氧化膜层的特性进行了研究。结果表明，随着电流密度的增加，微弧氧化膜层的增厚导致氧化电压增加。微弧氧化膜表面多孔，微孔的直径和烧结盘尺寸逐渐增加。膜层表面C、Si元素的相对含量随电流密度增加而增多，C元素在膜层表面呈均匀分布，膜层截面C元素主要集中在膜层外侧。膜层主要由SiC, SiO_2, θ-Al_2O_3, α-Al_2O_3组成, SiC相来源于石墨与SiO_2反应。随电流密度增大，膜层硬度增加。膜层耐蚀性呈先升高后降低的趋势，并在5 A/dm^{2}时膜层腐蚀速率最低。

关键词：微弧氧化；ZL108铝合金；电流密度；石墨；特性

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