Influence of silicon on growth mechanism of micro-arc oxidation coating on cast Al–Si alloy

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Micro-arc oxidation (MAO) is a plasma-assisted electro-chemistry method to prepare protective ceramic coatings on aluminium alloys. Alloy elements of the Al-alloy substrate, such as Si, Cu, Mg and Li, have effects on the microstructure and composition of the MAO coatings. Usually, silicon distributes in the cast Al–Si alloy substrate as small laths and they cover approximately 10% of the substrate surface. Therefore, their effects on the growth process and microstructure of the MAO coatings are worthy of notice. In the present study, oxide coatings with a thickness of 15–18 µm were prepared on the ZL109 Al–Si alloy by MAO. The phase content, surface morphology and element distribution of the coatings were investigated by X-ray diffraction, grazing incidence X-ray diffraction, scanning electron microscope, and electron probe micro-analysis respectively. The average hardness of the coatings was 622.3 ± 10.2 HV0.05. The adhesive strength of the coatings is 40.55 ± 2.55 N, and the adhesion of the coatings could be rated as 5B by tape test according to ASTM D3359-17 standard test methods, which indicated a high adhesive strength between the MAO coating and substrate. The effects of silicon laths on surface morphology and composition of the coatings were discussed, and a model was put forward to describe the growth process of the MAO coatings on cast Al–Si alloys. The authors believe that the high silicon content of the substrate has no adverse influence on the structure and properties of the MAO coating on the ZL109 alloy.

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1. Introduction

Micro-arc oxidation (MAO), also named as plasma electrolysis oxidation, is a plasma-assisted electrochemistry method that can be used to prepare protective ceramic coatings on aluminium alloys [1–4]. A key feature of the process is a plasma discharge that occurs at the metal/electrolyte interface when the applied voltage exceeds a certain critical breakdown value (typically several hundreds of volts) and appears as a number of discrete short-lived microdischarges moving across the metal surface [5–7]. After the MAO treatment, hard and well-adhered oxide coatings with excellent tribological performance and dielectric properties can be prepared on the metal surface [8–10]. It is thought that the MAO technology is an effective and promising surface strengthening method for aluminium and its alloys [11].

Cast Al–Si alloys, usually with silicon content $\omega_{\text{Si}} > 10\%$, are the most commonly used aluminium alloys in the modern automobile industry [12,13]. Surface protection is required for many parts, such as the piston, piston ring and connecting rod in the engine, that often encounter early failure caused by the surface abrasion and corrosion [14]. Many attempts to prepare MAO coatings on Al–Si alloys have been reported [15–17]. As the substrate has a high content of silicon and the areas covered by silicon laths take approximately 10% of the substrate surface, its effects on the MAO process and coating composition are worthy of notice. In previous studies, coatings on these alloys were considered as a mixture of Al–Si–O compounds dominated by $\gamma$-Al$_2$O$_3$ or $\alpha$-Al$_2$O$_3$ [16,18,19]. Small amounts of silicon compounds such as Al$_2$SiO$_5$ and mullite were found as well [16,20]. Wang et al. had made a model to describe the growth process of the MAO coatings [15]. However, they ignored a fact that the coatings grow towards the inside of the substrate even at the beginning of the MAO process. So in this paper, similar MAO coatings were made on the ZL109 alloy in a phosphate electrolyte. The effects of silicon laths in the substrate on the coating growth and composition were investigated and a new model was put forward to describe the growth process of the MAO coatings on cast Al–Si alloys.

2. Experimental procedures

The cast Al–Si alloy named ZL109, with a nominal composition of 11–13% Si, 0.5–1.5% Cu, 0.8–1.5% Mg and Al balance, was used as the substrate material. Rectangular samples (12 × 8 × 4 mm$^3$) were ground using 1000# SiC paper, based on our experience, this will normally deliver an average roughness of around 1 micron. Then the samples were cleaned with acetone and distilled water before the MAO treatment. For the MAO treatment, the specimen that was used as an anode was immersed in a solution of phosphate salt (0.6 mol l$^{-1}$ Na$_3$PO$_4$, pH = 8), while a stainless steel plate was used as a cathode. Electrolyte temperature was controlled under 30°C. The current density was in the range of 4–6 A dm$^{-2}$. The duration for the MAO treatment was 30 min. After the MAO treatment, samples were washed with distilled water and dried at room temperature. In order to evaluate the effect of Si on the microdischarge in the MAO progress, a pure aluminium sample containing 99.99% Al was also involved.

The phase contents of the MAO coating were determined by X-ray diffraction (XRD, D/max-RC, $i = 40$ mA, 4° min$^{-1}$) and grazing incidence X-ray diffraction (GIXD, X’ Pert PRO, $i = 35$ mA, 3° min$^{-1}$), both using Cu-K$_\alpha$ radiation operated at a voltage of 40 kV. The incidence angle for GIXD is 0.5°. The coating surface and cross-section micrographs were observed by JXA-8800R electron probe micro-analysis (EPMA). Element distributions in the MAO coating were also analysed. The hardness and adhesive strength of the coatings were evaluated using Shimadzu Vickers hardness tester, WP-2000 scratch tester and ASTM D3359-17 standard test methods for rating adhesion by tape test. 3M 610-1PK-25.4 mm tape (Scotch®) was used in the tape test. For the scratch test, the loading rate was 40 N min$^{-1}$, the probe speed was 4 mm min$^{-1}$ and the maximum load was 80 N sliding. The micrographs of the scratch test were observed by JSM-6380 scanning electron microscope (SEM). Owing to the low conductivity of the coating, the samples were sputter-coated with carbon prior to the EPMA and SEM observations.

3. Results

3.1. Phase analysis

The ZL109 alloy is a eutectic Al–Si alloy (alloys with lesser than 11.7% Si, the eutectic composition) whose microstructure contains coarse $\alpha$-Al dendrites and flake-like eutectic silicon phases according to the Al–Si phase diagram [21,22], as shown in figure 1. Si improves the fluidity and castability of aluminium [23].
Si phase distributions of ZL109 alloy, as shown in (a) and (b,c) at low and high magnification, respectively; (d) Al–Si phase diagram.

Figure 1. Si phase distributions of ZL109 alloy, as shown in (a) and (b,c) at low and high magnification, respectively; (d) Al–Si phase diagram.

Figure 2. Phase analysis of MAO coatings on ZL109 alloy in a solution of phosphate salt by: (a) XRD and (b) GIXD.

The combined area covered with silicon takes more than 10% of the substrate surface, and the size of silicon particles is in the range of several to several tens of microns.

The XRD pattern of the MAO coating on the Al–Si alloy is shown in figure 2a. Aluminium and silicon with a small amount of γ-Al2O3 can be identified. As the Al–Si alloy substrate used in this work is a typical eutectic structure of aluminium solid solution that contains small silicon particles, the authors believe that X-ray could probably penetrate through the thin MAO coating and the peaks of aluminium and silicon are most likely to come from the substrate. Therefore, GIXD is used to give a clear result, as shown in figure 2b. It can be seen that the peaks of γ-Al2O3 become sharper and clearer, while the peak strength of aluminium and silicon obviously decreases. This result confirms the authors’ inference and indicates that the coating is mainly composed of γ-Al2O3. In addition, small amounts of other phases, SiO2 (quartz) and Al2SiO5 are identified from figure 2b.

3.2. Surface, cross-section morphology and element distributions

Figure 3 shows the surface and cross-section micrographs of the MAO coating on pure aluminium (figure 3a) and the Al–Si alloy (figure 3b). Both of their surfaces, over which round pores distribute evenly, are a little rugged. But the surfaces are quite different in pore size and density. The pores on the Al–Si alloy are larger, with diameters of 3.61 ± 1.31 µm and a low density; while the pores on pure aluminium are smaller, with diameters of 1.06 ± 0.47 µm and a relatively high density. The diameters of pores are measured from surface micrographs of MAO coatings. Usually, it is believed that the formation of the pores is attributed to the electrical discharge phenomenon occurring on the sample surface when voltage applied during the MAO process reaches a critical value (up to several hundred volts). In this condition, local areas of the sample surface can be broken down by an instantaneous micro-arc/spark. When the micro-arc/spark extinguishes, a pore would be left. But the porosity and hardness of MAO coatings could be optimized by adjusting MAO parameters (current density, composition of electrolyte and oxidation time) [24], and further sealing treatment would also make up the porous defects of the MAO layer [25]. Zhu et al. [26] sealed the pores of MAO coatings with grease, and it was proved that
the sealed MAO coating exhibited a better fretting wear resistance and longer service life. Ivanou et al. [27] sealed the pores of MAO coatings with hybrid epoxy-silane formulation, the sealed MAO coating provided good corrosion resistance.

The cross-section micrograph and element distributions in direction of depth of the MAO coating on the ZL109 alloy are shown in figure 3c. It can be seen that the whole coating, with a thickness of 8–10 µm, is relatively dense and homogeneous in the direction of depth, which is quite different from the coating surface. There is no obvious crack in the coating. No discontinuous zone is observed between the coating and substrate. This implies that the MAO coating has high adhesive strength to the substrate. Figure 3d shows that the coatings on the Al–Si alloy are mainly composed of Al, O and Si with a trace amount of P, which is consistent with the XRD analysis.

3.3. Hardness and adhesive strength

The average hardness of the coating is $622.3 \pm 10.2 \text{ HV}_{0.05}$, which is about 7.9 times higher than that of the substrate ($79.2 \pm 1.2 \text{ HV}_{0.05}$). The coating is mainly composed of $\gamma$-$\text{Al}_2\text{O}_3$ and small amounts of SiO$_2$ and Al$_2$SiO$_5$. Student et al. [28] demonstrated that a proportion of 60% $\gamma$-$\text{Al}_2\text{O}_3$ in coatings exhibits high hardness. Krishna et al. [29] reported that hardness value of $\gamma$-$\text{Al}_2\text{O}_3$ phases is calculated to be 806 HV. The intrinsic hardness of the SiO$_2$ is slightly lower than that of Al$_2$O$_3$ [30], but the hardness values of Al$_2$SiO$_5$ is higher than Al$_2$O$_3$ [31]. Therefore, within the experimental scope, the high hardness of our MAO coatings could be attributed to the formation of $\gamma$-$\text{Al}_2\text{O}_3$. But the eventual hardness of the coatings depends on the proportion of these phases. The high hardness of the coatings proved that micro-arc oxidation has the potential to prepare wear-resistance coatings on Al–Si alloys.

The friction-load curve of the MAO coating on the Al–Si alloy is shown in figure 4a. The adhesive strength of the coatings is $40.55 \pm 2.55 \text{ N}$. The peak value is 43.1 N, which indicates that the MAO coating has high adhesive strength to the substrate. Figure 6 shows the micrographs of the scratch track of the
MAO coating on the Al–Si alloy. The coating is smoothed and the coating material is extruded to both sides along the track (figure 4a). At the beginning of the track, as shown in figure 4b, the surface pores of the MAO coating can still be seen. However, this surface character has gradually disappeared in the midst of the track, and the substrate is exposed finally (figure 4c). The edge of the track is shown in figure 4d. The coating material is piled at the track edge, and there is no large peeling off, which implies the coating has excellent toughness. Furthermore, according to the ASTM D3359-17 standard test methods for rating adhesion by tape test [32,33], three samples were tested and three faces of each sample were tested to avoid occasionality. The adhesion of the samples could all be classified as 5B, owing to the edges of the cuts which are completely smooth, and none of the squares of the lattice is detached (figure 5). 5B is the highest rank of adhesion strength.

These two methods both demonstrate excellent adhesive strength between the MAO coatings and ZL109 substrate which would be suitable for commercial applications. The in situ formation of MAO coatings promises the good adhesive strength to the substrate [34].

4. Discussion

The effects of alloy elements on the MAO process of aluminium alloys were continuously studied by researchers. Nykyforchyn et al. [2] found that element Li is helpful to enhance the hardness of the MAO coating and the total fraction of Cu and Mg must be at least 3.5%. However, independent phases containing these elements were seldom observed in MAO coatings. References [8,35,36] showed that small amounts of phases containing silicon, such as Al₂SiO₅, Al₄Si, and Al₆Si₂O₁₃ could be identified from the XRD patterns of MAO coatings on aluminium alloys, which implied the effect of silicon on the composition of the coatings. Compared with aluminium alloys with low alloy content, the oxidation process on cast Al–Si alloy is special, given that the mass fraction of silicon in the substrate is more than 10 wt.%. Many small silicon particles are distributed on the substrate of the Al–Si alloy. In other words, the combined area covered with silicon takes about 10% of the substrate surface. So what role would the small particles on the sample surface play in the MAO process? Can oxide coatings be formed...
on these silicon-covered areas? If it could, what structure and composition would this kind of oxide coating have? As the microdischarge is generated in a very small local area (with a diameter of 1–10 µm [6,37]), and its lifetime is very short, probably $t < 1$ ms [38], it is difficult to solve these problems by direct experimental observation. Therefore, a growth model of the MAO coating on Al–Si alloys was built by Wang et al. [15]. In their model, the voltage variation with treatment time and corresponding surface morphology and composition of the MAO-coated Al–Si alloys were considered. They believed that after the first stage of oxidation, namely the passivation stage, large micro-arc discharges first formed at the boundary of Al–Si. This happens when the voltage reaches a critical value owing to the tip/corner effect of electrical concentration on the localized surface where the interface of Al matrix and silicon grain exists. While passivation films grow towards the substrate in the passivation stage [39], there are some volume dilatations when Al and Si are transformed into their corresponding oxides (47% and 88%, respectively). So supposing that a surface layer of 10 nm thickness of the substrate was oxidized in the passivation stage, the tip height at the interface of different oxide areas would be only 4 nm, which is far smaller than substrate roughness (on an order of magnitude of microns [8,15,40]). So we believe that discharges cannot be generated by the tip/corner effect. Considering the surface morphology, phase content and composition of the MAO coatings, and comparing them with that of a pure aluminium, a new model to describe the growth of the MAO coating on Al–Si alloys is put forward. The MAO process was divided into three stages for succinctness, as shown in figure 6.
4.1. The passivation stage (I)

This is the stage before the applied voltage reaches the critical discharge potential. From reference [39], a passivation layer with a thickness of 6–20 nm can be formed on the exposed silicon crystals via chemisorption. A natural oxide layer on aluminium matrix, which is composed of amorphous Al₂O₃ with a thickness of 2–3 nm, also exists before passivation [6,41,42]. In the passivation stage, both of them will grow thicker and reach 10–15 nm by anodizing oxidation, as shown in figure 7a. The authors believe that there is no obvious difference in the thickness between the passivation oxide layers on aluminium matrix and silicon laths because the duration of this stage is very short (t₁ < 2 min [15]).

4.2. The stable oxidation stage (II)

This is the typical MAO stage. When the voltage reaches the critical discharge potential, the thin oxide layers formed in the passivation stage will be broken down, and many tiny sparks around the sample can be seen [43–45]. Electrical properties of the main substances of the Al–Si alloy surface are shown in table 1 (compiled from references [8,34]). It can be seen that the dielectric strength of silica is 1.5–2.5 times higher than that of alumina. Therefore, alumina layers on aluminium matrix will first be broken down as the voltage increases (figure 7b). In the local discharge area, the passivation films are melted at the instantaneous high temperature and the aluminium matrix will further be oxidized by element diffusion. When a spark extinguishes, the local film will be rebuilt with the melted oxide that is quickly cooled by the electrolyte. As a result, the oxide film grows into the substrate and the discharge potential increases with thickness of the film. When the discharge voltage of alumina film becomes higher than that of the silica film, the discharge locations will change.

From table 1, the conductivity of aluminium is much better than that of silicon. So the edges of larger silicon particles, namely the boundary between the alumina and silica layers, are closer to the aluminium matrix and become positions that electric current is easier to pass through. The discharge will first move to these areas where new Al–Si–O films, a mixture of alumina and silica, will be formed via oxidation and diffusion. Then the discharge positions will move towards the centre of the silicon particles as the Al–Si–O films grow. For smaller silicon particles, discharges may happen on its entire areas, and the Al–Si–O films will be directly formed, as shown in figure 7c. Finally, a homogeneous thicker coating can be formed on the Al–Si alloys, and the discharge positions will return to the surface of aluminium matrix.
Table 1. Summary of electrical properties of main substances on the Al–Si alloy surface [44,46].

| substances     | dielectric constant | electrical resistivity (Ω cm⁻¹) | dielectric strength (kV mm⁻¹) |
|----------------|---------------------|---------------------------------|-------------------------------|
| aluminium, Al  | —                   | 2.9 × 10⁻¹⁰                    | —                             |
| alumina, Al₂O₃ | 9.9                 | 10¹⁴                            | 10                            |
| silicon, Si    | —                   | ~10⁻⁶                          | —                             |
| silica, SiO₂   | 3.9                 | 10¹⁰–10¹⁴                      | 15–25                         |

because the discharge voltage of silica film becomes higher than that of the alumina film again, as shown in figure 7d.

The above-mentioned process may be repeated many times during the stage. The discharge voltage will gradually increase as the MAO coating grows thicker, as shown in figure 6. The fact that the pore size of the MAO coatings on the ZL109 alloy is larger than that on pure aluminium (figure 3) can be attributed to the existence of silicon. Because the discharges happen alternately in different local areas such as the aluminium matrix and silicon particles, the discharge area of the Al–Si alloys is at times smaller than that of pure aluminium, especially when silicon particles are the main discharge areas. So if the current density for both aluminium and Al–Si alloys is at the same level, the strength of an individual microdischarge for Al–Si alloys will be much higher than that of pure aluminium.

4.3. The final oxidation stage (III)

In this stage, the increase of the applied voltage starts to become slower. The number of sparks obviously decreases and the discharges gradually concentrate to the edge of the samples. Different substances in the MAO coating react further as the coating thickness increases. Usually, the thickness of silicon particles is several microns, a little thinner than that of the oxide film. So in areas where silicon particles are smaller, the aluminium matrix under the silicon particles will be oxidized when they are completely oxidized. Meanwhile, in areas of the aluminium matrix, the growing alumina films may reach the shallow-distributed silicon particles under the substrate surface. Both of the two functions promote reactions between silica and alumina. Moreover, owing to the diffusion effect caused by the repeated discharges, the composition transition between alumina and Al–Si–O layers gradually become more homogeneous.

In addition, owing to the repeated effects of melting and condensation in stages (II) and (III), the coating transforms from amorphous alumina to crystalline alumina. In the XRD analysis, the diffraction peaks of Al₂O₃ are relatively sharp, which indicates its high crystallinity.

5. Conclusion

(i) Oxide coatings with a thickness of 8–10 µm were deposited on the substrate of the ZL109 Al–Si alloy by MAO. The average hardness of the coating was 622.3 ± 10.2 HV₀₀₅, which was 7.9 times higher than that of the substrate. The high hardness was attributed to the formation of γ-Al₂O₃ in the coating. The surface of the coating was porous, and the pore diameter was 3.61 ± 1.31 µm. The coating matrix was homogeneous and with few defects. There was a high adhesive strength between the MAO coating and substrate. The adhesive strength of the coatings is 40.55 ± 2.55 N, and the adhesion of the coatings is classified as 5B.

(ii) Silicon particles in the Al–Si alloy substrate have great effects on the growth process, surface morphology and composition of the MAO coating. The MAO process was divided into three stages, namely the passivation stage, stable oxidation stage and final oxidation stage. After the passivation stage, local alumina layers on the aluminium matrix surface would first be broken down owing to their lower dielectric strength. With the discharge voltage gradually increasing, the local aluminium and silicon areas were alternately broken down, and the MAO coating grew towards the substrate and became thicker. The coating was composed of Al–Si–O compounds, with Al₂O₃ as the main phase and small amounts of other phases, such as SiO₂ or Al₂SiO₅. The formation of Al–Si–O compounds can be attributed to the element diffusion and reactions in the MAO coating when local coating areas were broken down. The authors believed that the existence of silicon particles in the substrate had no adverse influence on the growth and properties of the MAO coating on the ZL109 alloy.

Data accessibility. This article does not contain any additional data.
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