



The mechanism of PEO process on Al–Si alloys with the bulk primary silicon

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ABSTRACT

This study focuses on mechanism of ceramic coating on Al–Si alloys with bulk primary Si using plasma electrolytic oxidation (PEO) technology. Al–Si alloys with 27–32%Si in weight were used as substrates. The morphologies, composition and microstructure of PEO coatings were investigated by scanning electron microscopy (SEM) with energy dispersive X-ray system (EDX). Results showed that the PEO process had four different stages. The effect of bulk Si is greatly on the morphology and composition of coatings at first three stages. Anodic oxide films formed on Al and Si phases, respectively. When the voltage exceeded 40 V, glow appeared and concentrated on the localized zone of interface of Al and Si phase. Al–Si–O compounds formed and covered on the dendrite Si phase surface, and the coating on bulk Si, which was silicon oxide, was rougher than that on other phase. If the treatment time was long enough, the coatings with uniform surface morphologies and elements distribution will be obtained but the microstructure of inner layer is looser due to the bulk Si.

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1. Introduction

Cast Al–Si alloy is a kind of promising material used in automobile due to their high strength-to-weight ratio, excellent castability and good mechanical properties, etc. [1,2]. However, poor wear and corrosion resistance often decrease the lifetime of cast Al–Si alloy components. Thus, some surface modification or coatings on Al–Si alloy would be beneficial to the application.

Plasma electrolytic oxidation (PEO) is a kind of electrochemical surface modification technology to fabricate the ceramic oxide coatings on valve metals such as Al, Mg and Ti [3]. The PEO coatings represent excellent properties, such as high hardness, wear resistance, anti-corrosion and thermal stability [4–6].

However, the alloying elements, especially Si element have a great effect on the PEO process, structure and properties of ceramic coatings [7,8]. Nie and other researchers have studied on the structure, composition and properties of coatings formed on Al–Si alloys and the effects of silicon on formation of PEO coatings [9–12]. Krishtal [13] reported that if Al–Si alloy substrate contains great amounts of Si, the Si will prevent the reaction of aluminum

with oxygen. As a result, porous structure will increase in the ceramic coating, hardness and adhesion of coatings will decrease as well.

The silicon contained in Al–Si alloys referred in above papers exists as eutectic phase. However, when the content of silicon exceeds 12.5 wt.%, bulk primary silicon will appear in the Al–Si alloys. The growth process of PEO coating on these alloys is special, and the research of which is not reported yet.

In the present study, hypereutectic Al–Si alloys with bulk primary silicon were treated by PEO technology in silicate electrolyte. The coatings growth process, their morphologies and composition were investigated.

2. Experimental design

PEO experimental equipment consists of a pulsed AC sources, auto-control and automatic data collection system and an electrolyte container (Fig. 1). The Al–Si alloy samples (25 mm × 25 mm × 5 mm) were used as anode and the nominal composition of this alloy was 27–32%Si, ≤0.1%Mn, ≤0.3%Fe, ≤0.1%Cu and Al balance. All the samples were polished and cleaned to obtain a uniform surface. Silicate at a concentration of 20–40 g/L and alkali (NaOH) at 0.5–1 g/L were used for PEO process. A constant current density was set as 0.6 mA/mm², and the temperature of electrolyte was controlled below 35°C. A FEI

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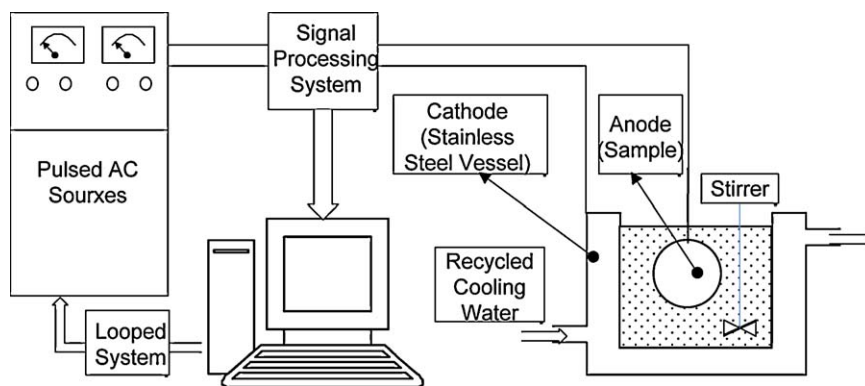


Fig. 1. Sketch of PEO equipment.

Quanta 200F field-emission scanning electron microscopy (SEM) with energy dispersive X-ray system (EDX) was used for analyzing the morphology of coatings and the element composition of surface and cross section of coatings as well.

3. Results

3.1. Metallurgical analysis of the Al–Si alloy substrate

The microstructure of substrate is shown in Fig. 2, which was obtained by optical microscopy. It can be seen that the Al–Si alloy is composed of the α -Al phase, the primary bulk β -Si and the eutectic ($\alpha + \beta$) phase with an interdendritic distribution. The size of primary bulk Si can reach about $0.1 \text{ mm} \times 0.3 \text{ mm}$.

3.2. Voltage variation during the PEO process

Fig. 3 shows the voltage variation with treated time during the PEO process, and there exists four stages according to changes in voltage and discharge phenomenon. A conventional anodic oxidation began at Stage I and the voltage increased rapidly to

40 V. The initial discharge appeared at stage II with lower rate of increase in voltage, and fine white glow distributed on the sample surface uniformly. At stage III, the voltage increased slowly from 80 V to 120 V. Microarcs with color of saffron were observed at this stage. With the PEO time prolonged, the size of microarcs increased and the number of them reduced. After 240 min, the voltage oscillated acutely and the auto-control system cannot keep the preset current density at the end of the PEO process. Several bright sparks with long discharge time appeared on the surface simultaneously.

3.3. The effect of PEO time on morphology and composition characterization

Fig. 4 shows the surface morphologies of the PEO coatings treated at different time. At the time of 10 min (Fig. 4a), the anodic oxide films with different morphologies formed on the α -Al, the primary bulk β -Si and the eutectic ($\alpha + \beta$) respectively. Coatings formed on the bulk primary Si have a greater volume expansion (Fig. 4b), and show high brightness region in the SEM photo. At the time of 60 min, the coatings deposited on the α -Al and the eutectic ($\alpha + \beta$) are uniform, but the rougher coatings were observed on the

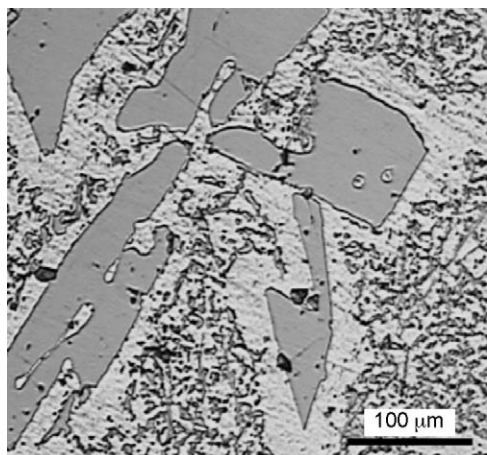


Fig. 2. Optical microstructure of Al–Si alloy.

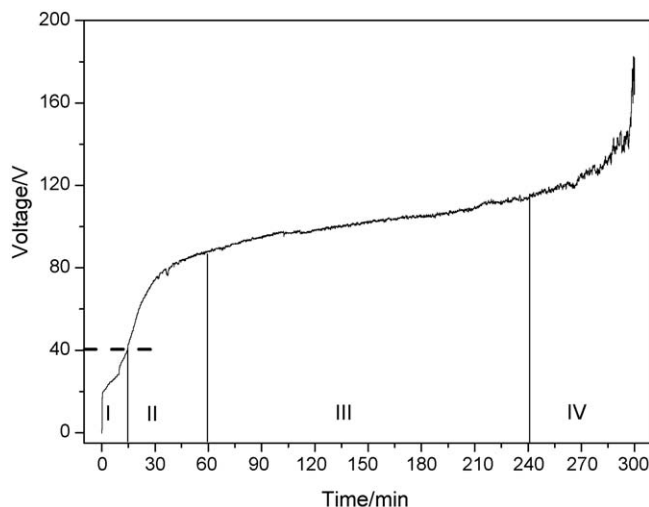


Fig. 3. Curve of voltage vs. treatment time during the PEO process.

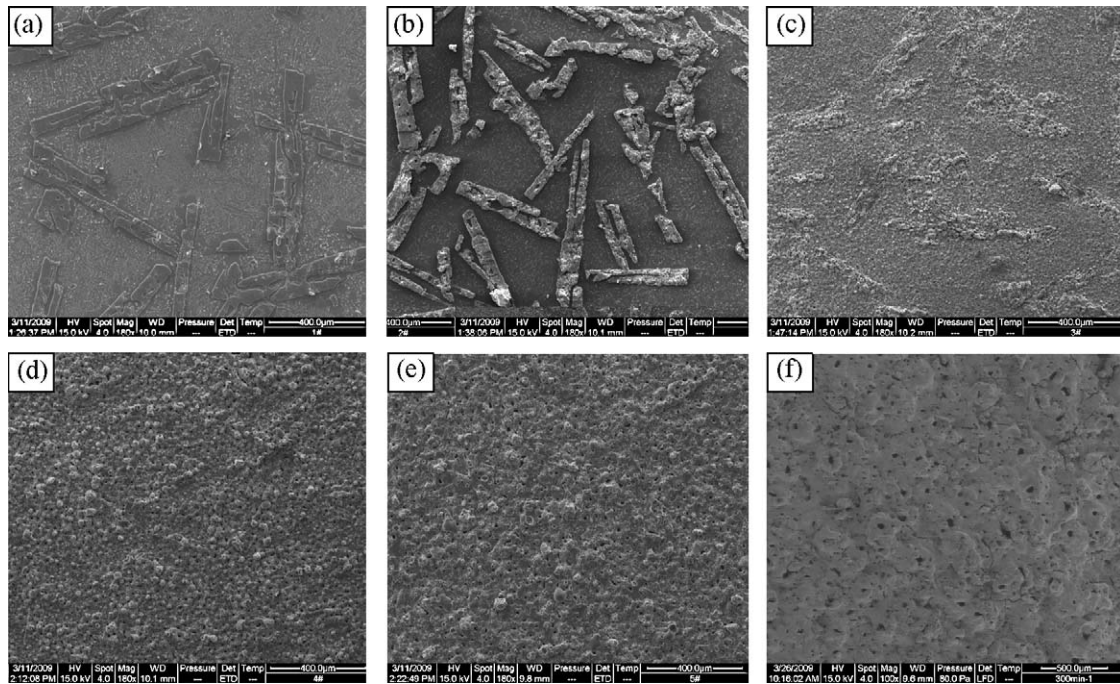


Fig. 4. Surface morphologies of the PEO coatings treated at (a) 10 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min and (f) 300 min.

primary bulk Si (Fig. 4c). With the PEO time increasing, the uniformity was improved as it is shown in Fig. 4d and e, and at the end of PEO process (Fig. 4f), it is very hard to distinguish the effect of bulk primary Si on the surface morphology.

Furthermore, the compositions of coatings were analyzed by EDX to determine the products of PEO coatings obtained under the different stages. At the time of 30 min (Fig. 5), the product formed on the bulk primary Si is silicon oxide only which was shown in Fig. 5c. The Al–Si–O compound was obtained on the surface of the other two phases (Fig. 5d and e), but the content of Si in the coatings on the eutectic ($\alpha + \beta$) phase is higher than that on the α -Al. At 60 min (Fig. 6), the eutectic ($\alpha + \beta$) region cannot be distinguished and the bulk primary Si region was selected to be analyzed. The product formed on region 1 is almost silicon oxide (Fig. 6b) and is alumina (Fig. 6c) mainly on region 2. The borderline of the bulk primary Si becomes illegible, but the morphology of PEO coating formed on Si is rougher than that formed on Al.

When processing time reached 120 min, it is hard to distinguish the different regions from the surface morphology (Fig. 7a). The results of surface element distribution show that O and Si elements distribute on the surface selectively (Fig. 7b and c), but Al element is non-uniform, which due to the existence of the bulk primary Si, that is the black areas in Fig. 6d. It is distinct that O element in the coating comes from the oxide product including silicon oxide and alumina, Si element comes from substrate and SiO_3^{2-} , and Al element comes from substrate. Therefore, the morphology is uniform but the produce formed on the bulk primary Si is still silicon oxide at 120 min.

In order to confirm the conclusions above, which is only silicon oxide was formed on the bulk primary Si, the elements distribution on cross section was analyzed (Fig. 8). The results revealed that silicon oxide formed mainly on the bulk primary Si,

while alumina containing little silicon oxide formed on the other regions.

Fig. 9 shows the morphology and elements distribution of the surface of PEO coating at 300 min. At this time, all of the elements including O, Si, and Al distribute on the surface. It indicates that the bulk primary Si in the substrate has less effect on the composition of PEO coatings at the last stage of PEO process.

4. Discussion

Our results of the voltage variation, surface morphologies and the EDX analysis demonstrated a model of coating growth on Al–Si alloy with the bulk primary Si by PEO technology.

At the stage of conventional anodic oxidation, the voltage increased rapidly and passive films formed on the surface of three phases respectively (Fig. 10a). Due to the different properties of electrochemistry of Al and Si, a thin and dense film was formed on α -Al matrix but a porosity oxide film was formed on Si phase [14]. Furthermore, the PBR (Pilling-Bedworth Ratio) of Al (1.28) is lower than that of Si (2.22), so the film with a non-uniform surface morphology (Fig. 4a) was formed on the sample.

With the voltage increasing, the electric field strength in oxide film reached a critical value and discharges appeared at some positions of the interface of Al and Si firstly, which was due to the tip or marginal effect of electrical concentration (Fig. 10b). At the region of discharge, Al–Si–O compounds were formed because Si, Al, silicon oxide and alumina were melted and mixed at discharge channels with high temperature (above 3000 K at least) [3]. Thus the boundary of Al–Si was hard to distinguish, even part of dendrite Si was covered by Al–Si–O compounds (Fig. 4b). Gradually, several sparks were observed on α -Al matrix and bulk Si region, and alumina and silicon oxide were formed, respectively.

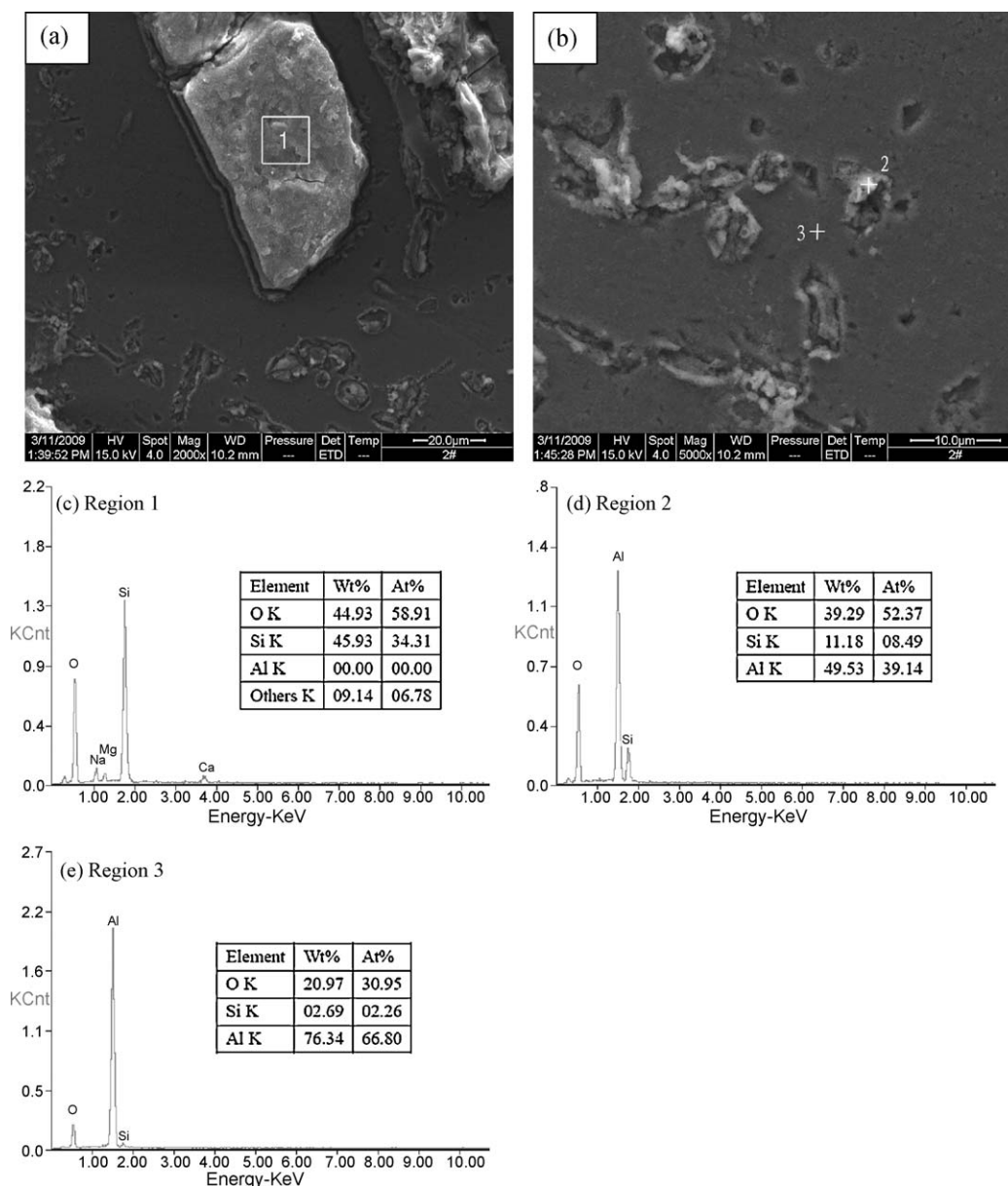


Fig. 5. EDX analysis of PEO coatings at 30 min: (a and b) the SEM micrographs, (c) EDX analysis from region 1, (d) EDX analysis from point 2 and (e) EDX analysis from point 3.

At stage III (Fig. 10c), microarcs were generated and distributed over the whole surface of the sample. All dendrite Si was covered thoroughly and the morphology of coating on it was similar to that on the α -Al matrix. The growth process of coatings on both phases above was uniform. But there were larger discharge spots on the bulk Si regions which was because of lower melt point, lower permittivity and more porosity (white circles shown in Fig. 10c) of silicon oxide and Al–Si–O compounds. The feature of coating could be observed in SEM analysis (Fig. 6a). With the increasing of PEO time, the areas of silicon oxide shrunk and the surface morphology of coating became uniform gradually. The reasons are follows: firstly, the process of products forming is due to breakdown discharging, melting at high temperature and pressure, and spherical products formed and quenched by the electrolyte, which results in epitaxially lateral overgrowth of products. Secondly, Al

element in electrolyte from dissolution of alumina and ejection from discharge channels was involved in the PEO reaction and deposited on the bulk Si regions [15]. Therefore, if the PEO time was long enough (Fig. 11), which was decided by the size of bulk Si, the surface morphology would be uniform. Comparing Figs. 7 and 9, Al, Si and O element distributed over the whole surface at the last stage of PEO, and there was no region with less Al element especially (Fig. 9d). The outer layer composition of coating was mainly influenced by electrolyte, while the effect of substrate was less. But the effect of bulk Si was proved by cross section photograph as shown in Fig. 8. The porous microstructure remained in the inner layer on the bulk primary Si while the PEO coatings were dense on the Al and dendrite Si. This meant the size of particles was a key factor of the microstructure and properties of PEO coatings formed on Al–Si alloys by PEO technique.

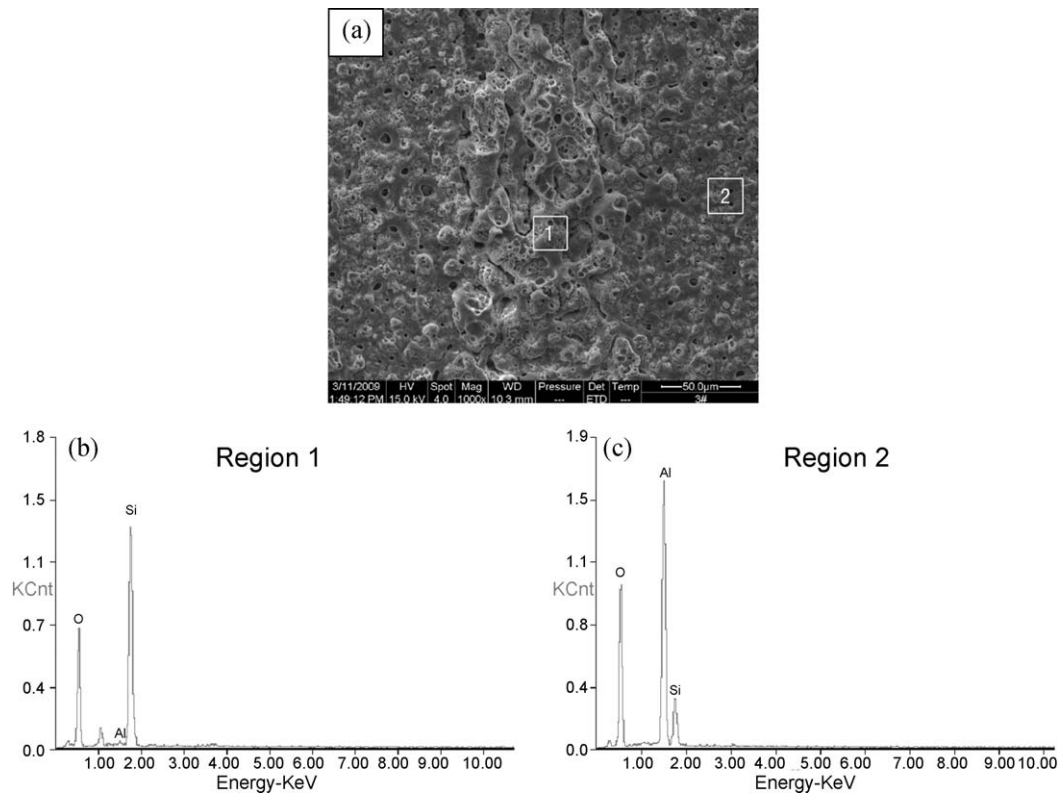


Fig. 6. EDX analysis of PEO coatings formed on Al-Si alloy at 60 min: (a) the SEM micrograph, (b) EDX analysis from region 1 and (c) EDX analysis from region 2.

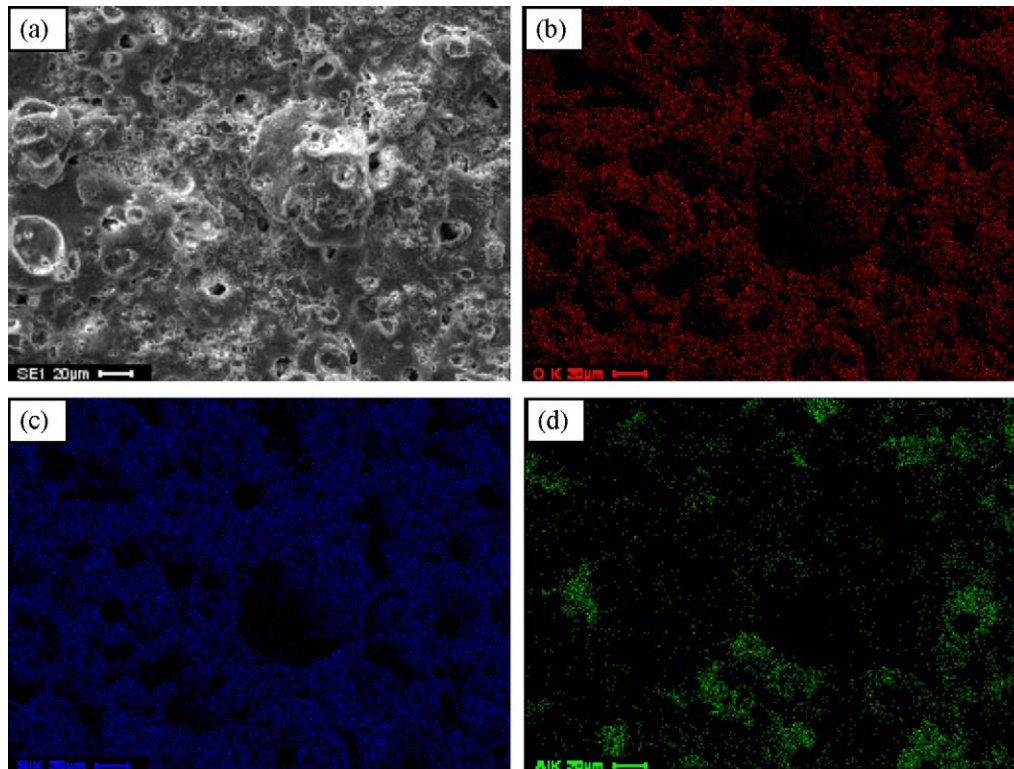


Fig. 7. EDX analysis of PEO coatings formed on Al-Si alloy at 120 min: (a) the SEM micrograph, (b) O element distribution, (c) Si element distribution and (d) Al element distribution.

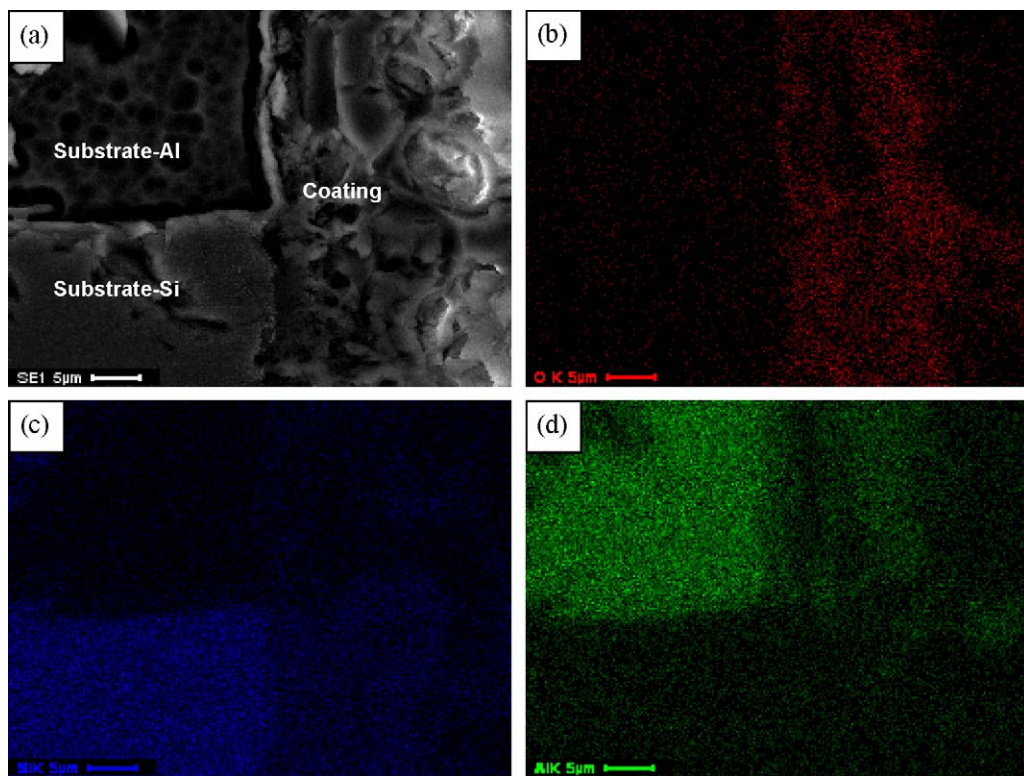


Fig. 8. EDX analysis of cross section formed on Al-Si alloy at 120 min: (a) the SEM micrograph, (b) O element distribution, (c) Si element distribution and (d) Al element distribution.

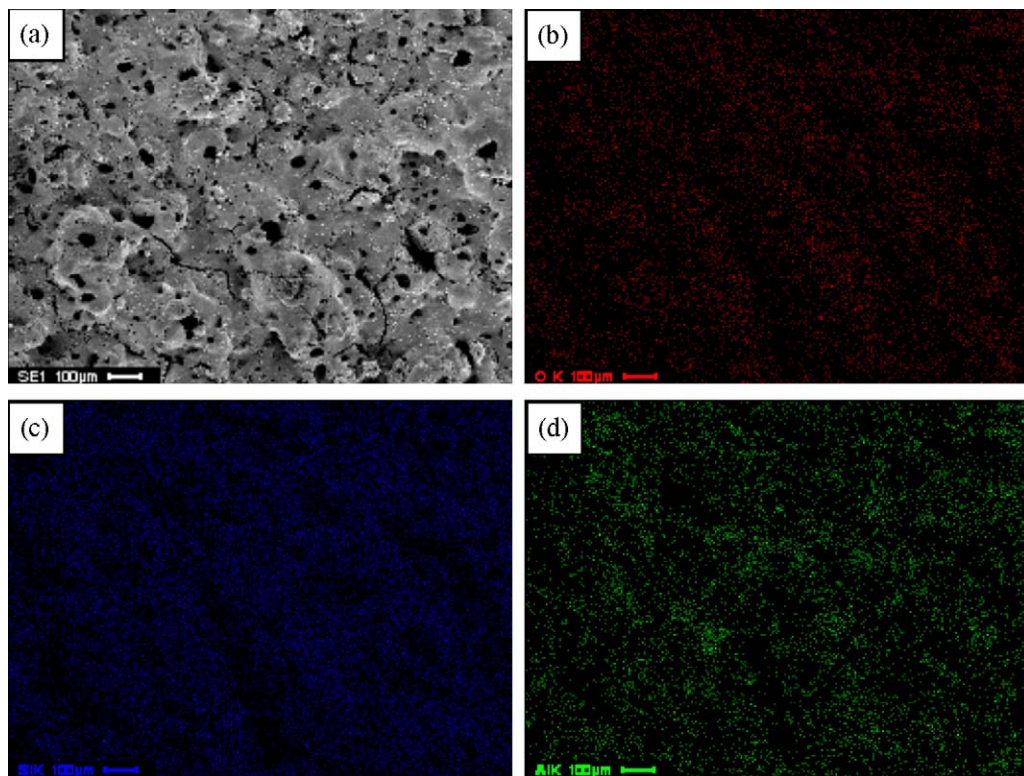


Fig. 9. EDX analysis of PEO surface formed on Al-Si alloy at 300 min: (a) the SEM micrograph, (b) O element distribution, (c) Si element distribution and (d) Al element distribution.

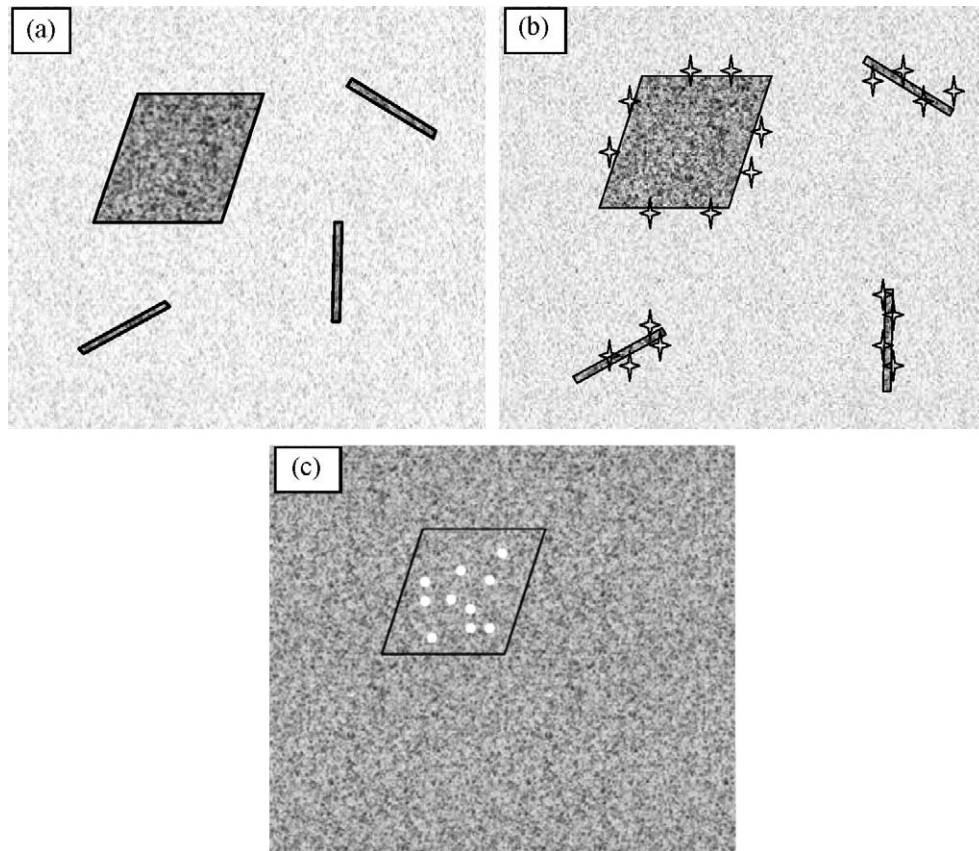


Fig. 10. Structure sketch of PEO coatings growth model on Al-Si alloys (a) stage I, (b) stage II and (c) stage III.

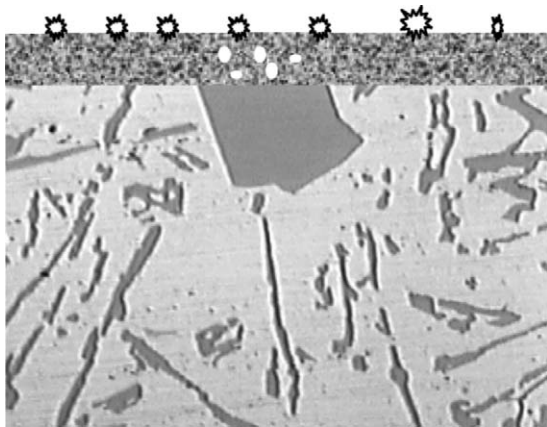


Fig. 11. The typical cross section sketch of coating on Al-Si alloys at the end of PEO process.

5. Conclusions

The model of coatings growth on Al-Si alloys by PEO technique was investigated. In conditions of this research, the process of coating growth had four different stages. At the first stage, anodic oxide films with different characters formed on Al and Si phases, respectively. Then glow appeared and concentrated on the local zone of interface of Al and Si phases. Porous Al-Si-O compounds were formed and covered on the dendritic Si surface. At stage III, PEO coatings were formed on the surface of Al-Si alloy, but the surface morphology on bulk Si was rougher than that on other regions. The products were silicon oxide and Al-Si-O compounds

(including alumina) respectively. At the final stage of PEO process, the coatings with uniform surface morphologies and element distribution were obtained. Because of the exist of bulk Si, it needs longer process time to obtain uniform coatings and the micro-structure of coating is looser in inner layer.

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