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An investigation about the evolution of microstructure and composition difference between two interfaces of plasma electrolytic oxidation coatings on Al

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^c College of Mechanical Engineering, Yanshan University, Qinhuangdao 066004, PR. China ^d Thermal processing technology center, Illinois Institute of Technology, Chicago, IL 60616, US **Abstract:** The plasma electrolytic oxidation (PEO) coatings were fabricated on AA1060 aluminum alloy at a constant current density of 4.4 A/dm². The images of discharge sparks and voltage-time response were recorded during the PEO process. The characteristics of the two interfaces of coatings were investigated as a function of PEO processing time by using X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS). Hundreds of coatings were detached from the substrate by an electrochemical method and ground into homogeneous powders to carry out differential scanning calorimeter (DSC) and further XRD qualitative test. In addition, matrix-flushing method was employed to quantitatively measure the content evolution of phase compositions of Al-based detached PEO coatings. The distribution rule of amorphous phases in the PEO coatings was investigated by thickness-reduction method for the first time. Based on the experiments above, gaining an insight into the formation, distribution and evolution of the amorphous and crystalline phases in the PEO process.

Key words: Plasma electrolytic oxidation; Amorphous phase; Crystalline phase;

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Coating/substrate interface; Elemental and phase compositions

1. Introduction

Aluminum and aluminum alloys have been focused much of attention in an extensive range of manufacturing industries currently, particularly in automotive industry, aerospace, computer industry and electronic communications[1, 2]. However, the relatively poor corrosion and wear resistance of aluminum and aluminum alloys have limited their wider application[3, 4]. Plasma electrolytic oxidation (PEO), also named micro-arc oxidation (MAO), is a branch of plasma electrolysis techniques [5]. It is a relatively new electrochemistry surface modification technique in which plasma discharge sparks are generated at high applied voltage, and ceramic coatings could be in-situ formed on the surface of Al, Mg, Ti and other valve metals with improved thermo-mechanical, corrosion and wear resistance performances compared with the conventional anodizing technique [6, 7]. The technique involves intricate combination of electrochemical, thermochemical, plasma-chemical and metallurgical processes[8, 9], so that the underlying mechanisms of plasma discharge and coating formation are still not well understood although many PEO studies have existed in the research literatures, even accordingly high-speed photography and microscopic observation technology have been employed to obtain higher-quality and higher-frequency pictures of discharge sparks in the PEO process[10, 11]. As a consequence of the research limitation above, it has been an important and scientific research method that applying other information to reverse inference the discharge process and the growth mechanism of PEO coatings, such as optical emission spectra (OES), voltage-time (or current-time) curve, the structures and phase compositions of the coatings of different time points, the element-tracking method and so on[8, 12-15]. By the above methods, some conclusions can be drawn about the main elements that ever participated in the reactions in different periods, and the main chemical reactions may be involved in the different stages, and the elemental

distribution profile of PEO coatings. However, those complex physical reactions (such as melt, solidification, phase transformation, etc) that have ever taken place in PEO process and the major locations of these reactions are still undefined.

It is obvious that PEO also is a process of dynamic equilibrium which is affected by electrolysis conditions [16-18]. To be specific, PEO coatings are composed of the elements from the electrolyte and the valve metal from the substrate owing to plasma electro-chemical, thermo-chemical, and some other kinds of reactions, the different electrolysis conditions can lead to different reaction processes and final results. However, most of the research results were focused on the coating/electrolyte (C/E) interface, i.e., the upside of the coating, because of the restriction of technology. Recently, the majority of methods that are used to observe and examine the coating/substrate (C/S) interface, i.e., the underside of the coating, are made through grinding and removing the outer layer of the coating or chemically etching the substrate in a hot sodium hydroxide solution with high concentration [19-21], but it is almost impossible for the real or original profile of the interface to be obtained due to mechanical or chemical damage of the coating during the preparation process of the C/S interface. Recently, our research group has developed an electrochemical process to detach the coating from its substrate, in this way, the coating morphology can be kept complete because a room temperature and neutral NaCl aqueous solution is employed in the electrochemical coating detaching process[3, 22]. There are already massive researches about the evolution of C/E interface over time, but the researches which paid attention on the differences between C/E interface and C/S interface are very few.

Moreover, the connection between phase compositions and morphological changes is ignored by us. With the development of PEO process, the influence of phase compositions mainly reflects in the following two aspects. One is the evolution of the C/E interface and C/S interface of PEO coatings over time, the other one is the differences between C/E interface and

C/S interface with PEO treatment time. Generally, the phase compositions of PEO coatings are rather complex, the PEO coatings are not only composed of crystalline phases (CPs), but also composed of a certain amount of amorphous phases (APs). The amorphous peaks which represent amorphous phases are like a steamed bun, typically appearing in the low angle of XRD spectrum and have the charcteristic of overlapping peaks [23, 24]. The formation and evolution of the phase compositions in the coatings will affect the morphology features of the coatings undoubtedly. K. Tillous et al. have studied the characteristics of distribution of crystalline phases in the PEO coatings on aluminium and its alloys [25]. There is a rich body of studies showing the existence of AP, but the AP, as a momentous part of coatings component, has not been revealed exactly in the specific content, distribution, transformation, elementary composition and the function of the forming process of PEO coatings. Therefore, it is significant for us to investigate these aspects to better understand the discharge and growth mechanisms of PEO coatings.

In the present work, systematic investigations were performed on the elemental compositions and microstructures of the C/E and C/S interfaces of different PEO treatment time points and the variable rule of element distribution difference between the two interfaces over time. Above all, in order to achieve the basic requirement of differential scanning calorimeter (DSC) test and quantitative measurement of phase compositions including APs, hundreds of PEO coating samples of each time point were detached from the substrate and ground into powder samples. The specific contents of phase compositions of the PEO coatings were quantitatively measured by using the matrix-flushing method [26], which are more accurate than estimated results before. In addition, the crystallization behavior of amorphous phases of Al-based detached PEO coatings is investigated by DSC and XRD for the first time. The distribution rule of amorphous phases in the Al-based PEO coatings is investigated by thickness-reduction method for the first time. Then the generation, content evolution and distribution rule of amorphous

phases in the process of PEO coatings are attempted to explain in the paper. In the process of discussion, we try to build the relationship between various representation information as far as possible. Based on the investigations above, the growth mechanisms of the PEO coatings were further analyzed and understood.

2. Experimental

2.1. Preparation of PEO coatings and voltage data acquisition

A sheet of AA1060 aluminum alloy (0.05% Cu, 0.03% Mn, 0.03% Mg, 0.05% Zn, 0.03% Ti, 0.25% Si, 0.35% Fe, 0.05% V, and Al balance) was cut into specimens with dimensions of 15 $mm \times 15 mm \times 2 mm$ as the substrate material for the PEO treatment experiments. Before the PEO treatment, all the specimens were ground successively with 600, 800, 1200 and 2000 grit emery sheets. Then the specimens were ulstrasonically cleaned with acetone, ethanol and distilled water successively, then dried in a warm air system. The PEO treatment was carried out in a home-made PEO experimental setup with the characteristics of a postive/negative potential pulse amplitude ratio of 5, a frequency of 50 Hz and a duty ratio of 50%. A simple PEO electrolyte with 2 g/L NaOH and 8 g/L Na₂SiO₃·9H₂O was used to investigate the growth mechanism of PEO coatings. The PEO processes were performed with a constant current density of 4.4 A/dm^2 and the electrolyte temperature was maintained at $30\pm 2^{\circ}$ by a circulating cooling system. The distance between the specimens and the metallic cathode is invariable, and the location of specimens remain unchanged in the electrolyte. For a series of PEO specimens, the PEO treatment time points were 1, 2, 5, 10, 15, 20 and 30 minutes, respectively. The voltage/current data were recorded by using a WaveScan 2.0 acquisition unit with a sampling interval of 0.9 ms. The plasma discharge images were taken by a Canon EOS 60D DSLR (18K pixels CCD, EF 50mm f/1.4 USM lens and shutter speed 1/5000 second) during the PEO process.

2.2. Detachment of PEO coatings from substrate

A series of PEO coatings were detached from aluminum alloy substrate by using an electrochemical method in neutral aqueous sodium chloride solution with the concentration of 1 mol/L [3, 27]. After detachment, the coatings were soaked in deionized water to remove the NaCl particles which adhering to the coatings, and then dried in the drying vessel.

2.3. Characterization of thickness, morphology, elemental and phase compositions of coatings data

The thickness values of coatings were measured by using an eddy current coating thickness gauge of type CTG-10 with a measurement accuracy of $\pm 0.1 \,\mu\text{m}$. Ten different locations were measured for each specimen and the average thickness of the coatings was based on the ten thickness values. The morphologies of outer surface, C/S interface and cross-section, and the elemental composition of PEO coatings formed for different time points were observed and measured by using a scaning electron microscopy (SEM, Hitachi S-4800) equipped with an energy-dispersive X-ray spectroscopy (EDS). Study on the phase composition of coatings was performed by using a X-ray diffractometer (XRD, D/MAX-rB) with Cu Ka radiation at 60kV and 40mA with step of 0.02° and a scanning rate of 2°/min over a 20 range between 10° and 80°.

2.4. Crystallization of amorphous phases and quantitative phase analysis

A mass of detached coating samples formed for PEO 30 minutes were ground into homogeneous powders with grit size of 0.1µm. The powders were divided into five equal parts, for two parts of experiments below. The first part of the experiments was treated in a NETZSCH SAT449C differential scanning calorimeter (DSC), its maximum service temperature is 2000 K and its heating rate is 40 K/min. Based on the DSC curve above, three of four were heated to 1250, 1400 and 1723 K at the same heating rate of 40 K/min, respectively. And then cooled to room temperature for the further XRD phase research. All the heat treatments were tested under

an argon environment. The rest one of four powdery samples without any processing just was just used as a comparing group.

In order to study the content change of phase compositions with prolonging the PEO treatment time, four time points were selected, i.e., 5, 10, 20 and 30 min. Hundreds of PEO coating samples of four different time points were detached from the substrate and ground into homogeneous powdery samples. The powdery coating samples were treated in conventional drying technology and marked as "D". The XRD matrix-flushing method was used to quantitatively measure the content of phase compositions of PEO coatings obtained at the 5, 10, 20 and 30 min, respectively. Each powdery XRD sample weighs 100 mg, including 80 mg PEO coating powders and 20 mg magnesium oxide powders with the purity of 99.99% as the flushing matrix. The two types of oxide powders were mixed together and ground to get homogeneous samples with grit size of 0.1µm. The four powdery samples were named D-5, D-10, D-20, D-30, respectively. In addition, the distribution rule of amorphous phase in the PEO coatings was investigated by layer-by-layer XRD determinations.

Results and discussion

3.1. Time relationships of PEO voltage/coating thickness /discharge pictures

All the PEO experiments are performed at a constant current of 4.4 A/dm², the voltage/coating thickness-time response curves and the morphological pictures of discharge sparks of specimen surface are shown in Fig.1. According to the change trend of voltage and the morphology feature of discharge sparks, it can be known that the PEO process consists of four stages in this case[8]. In stage I where the breakdown voltage is not yet reached, there exists an initial rapid voltage rise, principally involving the loss of metallic luster of the substrate surface and the formation of a white initial insulating oxide film due to rapid electrochemical dissolution and passivation reactions of the substrate alloy in a way similar to the traditional anodizing[28,

29]. The voltage rises is at a rate around 30 V/s at the this stage which lasts 14 seconds. In the second stage, the voltage rise starts to decrease markedly at ~406V, accompanied by a great number of white fine active discharges, bubbles and acoustic emission activities [30]. The stage lasts about 3 minutes from 14s to 204s, the rate of voltage rise is around 0.25V/s. In the meantime, the color and size of discharges become light yellow and larger, respectively. In stage III, as voltage continues to rise, the rate of voltage rise slows down further, around 0.069 V/s, its duration is about 13 minutes from 204s to 1004s. Meanwhile, the color of plasma discharges changes from light yellow to orange yellow, the size becomes larger, and both number and activity of discharges decrease further with time, accompanying with a lot of gas bubbles on the surface. The distribution state of spark discharges become non-uniform from the whole surface to the district density. In stage IV, the rate of voltage rise becomes even slower than stage III, only about 0.025 V/s, the voltage which is needed to maitain a constant current density tends to approximately constant. This stage is characterized by much larger, less, deeper yellow, more uneven and slower moving discharges than ever. Meanwhile, the more intense gas evolution is accompanied by relatively loud noise can be clearly observed. The variation of average PEO coating thickness with time is also depicted in Fig. 1. It can be seen that the coating thickness increases with time, but not linearly. The growth rates of the coatings in thickness at the four stages are 4.29, 2.30, 1.42, 0.53 µm/min (based on Fig.1), respectively. And there is a gradual downward trend in thickness rise rate. Especially, it is noted that the growth rate of thickness is not parallel to the the growth rate of voltage although the voltage with current is the driving force for the coating, which can be explained that there is a direct relationship between the voltage rise and compact inner layer thickness in the late period of the PEO process[27].

3.2. Outer and inner surface morphologies and elemental compositions

The outer and inner surface morphologies, i.e. the morphologies of coating/electrolyte (C/E)interface and coating/substrate (C/S) interface of PEO coatings obtained at different time points are shown in Fig. 2. In addition, the C/S interface means the underside of the coating stripped from the substrate with the electrochemical method. For the coating obtained at 1 min (named T-1, Fig. 2(1), and so on), the outer surface of coating is relatively smooth due to the thin and compact coating in spite of some fine pores, which can be attributed to that the oxygen gas evolution activities [19]. At this point, the corresponding morphologies of C/S interface with two different amplification multiples are shown in Fig. 2 (4) and (5). It can be seen that the inner surface of T-1 is also relatively smooth with the characteristic of small hemispherical oxides of about 0.7-0.8 μ m in diameter. As shown in Fig. 2(6) and (7), the outer surface morphology of T-2 is not so smooth as that of T-1 and many open pores of 1-3 µm in diameter can be observed on it. It can be seen from Fig. 2 (9) and (10) that the inner surface morphology of coating T-2 is also not so smooth as that of coating T-1 and has some small hill-shaped bulge structures on it, but has not any open pores like those of outer surface. In addition, it is notable that all the hill-shaped bulge structures are composed of a number of small balls like those shown in T-1 and T-2, which indicates that these small balls are the basic units in terms of microstructure to form the inner surface morphology of the PEO coatings, and their average size seems constant basically.

With increasing of the PEO time and the coating thickness, the voltage which needed to maintain the constant current density is incremental. Meanwhile, the number of weak sites decreases and the difficulty of dielectric breakdown increases because the plasma discharges are generated by dielectric breakdown through weak sites in the coatings[31], leading to an increase in the size of pores (Fig. 2) and the applied voltage (Fig. 1). However, the rise rate of voltage is much lower than that of coating thickness with time, which is attributed to the increase of the porous outer layer thickness and basically constant thickness of compact inner coatings[27]. With

the increase of applied voltage, the difference of structure and morphology between two interfaces are more obvious. On the one hand, more and bigger micro-cracks can be observed on the outer surface, which indicates that the formation and propagation of micro-cracks were continuously proceeding with time. The phenomenon could be attributed the following two reasons. Firstly, the increase of coating thickness will produce bigger residual stresses, promoting the formation and propagation of micro-cracks. Secondly, the increase of input energy will cause higher instantaneous temperature and temperature fluctuation in the coatings, so that the molten, sintering, solidification and diffusion process of the coating materials proceed more unevenly at different locations in the coatings, promoting the formation and propagation of micro-cracks. On the other hand, the pores are continuously changing in number and diameter with the increase of applied voltage and coating thickness. As is shown in the Fig. 2, the number of pores is decreasing but the average diameter of pores is increasing with time. This is due to the intenser activity of oxygen gas evolution with time [19].

Meanwhile, it can be noted that the area of smooth melt-solidification regions (marked "A") where near the pores is gradually decreasing and the area of rough reaction-sintering (marked "B") like "stick-like" is gradually increasing with prolonging the treatment time, which may be due to the secondary reactions between the molten alumina products on the surface and the electrolyte of silicate component [19]. More specifically, under the condition of sustained input energy, the oxide products in coatings have interaction with surrounding species in the electrolyte to form Al-Si-O phase (so-called type A discharges)[32]. The marked difference, however, is that the average size of bulge structures on the inner surface gets larger with PEO time, but the average size of hemispherical oxides microstructurs on the bulge structures is still roughly the same - the diameter of small spheres is still about 0.7-0.8 µm. The bigger bulge structures indicate that some intense reactions which are unable to in-sute observe have been occuring in the

C/S interface and going deeper into the substrate during the PEO process. The transmission electron microscopy (TEM) results showed that there is always a thin ($<1\mu$ m) amorphous alumina layer at the boundary next to the metal substrate, which is deduced that the C/S interface with hemispherical oxides is composed of the direct PEO products resulting from plasma discharges occurring at the substrate surface and the size of hemispherical oxides represents the size of the plasma discharge areas here[3, 27].

The Fig. 2 (3) is the EDS result from the selected area of C/E interface of T-1, Fig. 2 (8) is the EDS result from the selected area of C/S interface of T-1. Similarly, Fig. 2 (13) is corresponding to the C/E interface of T-10, and so on. The EDS results suggest that the C/S interface basically consists of Al and O element, and a small amount of Si (ignoring impurity elements). In addition, the chemical composition of the C/S interface with large time-span is relatively stable (T-1, T-10, T-30), its content still stays relatively constant, which indicates that the elemental composition of C/S interface is stable and changes little with prolonging treatment time. The marked difference, however, is that the chemical compositions of C/E interface of different time points show an obvious variation. In particular, the content of silicon element appears increasing with time. For instance, the silicon content of C/E interface of T-30 is much higher than those of the former two C/E interfaces. If the elemental compositions of material have something changed, which will undoubtedly affect the morphology of specimen. Therefore, it can be known that the difference of chemical composition of the C/E interface is corresponding to the variation of microscopic features. In conclusion, there are differences between the C/S interface and C/E interface about microstructures and elemental compositions, and the difference will become more and more apparent over time.

3.3. Cross-sectional images, and element distribution law

Cross-sectional images and EDS elemental section-distribution of the coatings of four time points are shown in Fig. 3. It can be seen that the coating thickness increases significantly with time, which is basically consistent with the coating thickness curve which presented in Fig. 1. The EDS results show that the contents of Al and O corresponding to the four time points are roughly evenly distributed throughout the coatings. However, it is noteworthy that the silicon element show a homogeneous distribution from the C/S interface to the C/E interface in specimens T-5, T-10 and T-20. But the content of Si next to C/E interface is obvious higher than that of C/S interface in the specimen T-30. The distribution rule of silicon element is consistent with the results of Fig. 2 in certain degree, which is deemed that there is a larger amount of elements containing silicon participating in the reactions on the C/E interface compared with the C/S interface during the PEO process.

3.4. Phase compositions of the coatings

It is known that when the X-ray pulse passes through a thin-film material, its intensity decreases in a exponential decay relationship with the thickness, as given by equation (1)[33, 34]: $I = I_0 e^{-\mu\rho z}$ (1)

where μ is mass absorption coefficient, *I* is the intensity of X-ray after absorption, I_0 is the intensity of X-ray before absorption, ρ is the density of thin-film material, *z* is the thickness of thin-film material. Therefore, a large amount of X-ray can penetrate the coatings to target the substrate easily because the PEO coatings are thin. In order to eliminate the interference of substrate composition on coating phase composition analysis, the coatings without substrate were obtained by using the electrochemical method which have been mentioned at the experimental section. The XRD spectrum of the T-30 coating without substrate is shown in Fig. 4. It is evident that besides some crystalline phases mullite, γ -Al₂O₃ and α -Al₂O₃, there is a substantial fraction of AP, indicated by the broad background peaks like a steamed bun and lots of overlapping peaks

within a 20 angle range from 13° to 40° approximately. Theoretically, the formation of amorphous state is an inherent feature of all the molten. The AP is inevitable to form once the cooling process of molten is insufficient, otherwise, it is a violation of the third law of thermodynamics[35]. To be specific, the molten material have a huge temperature difference in the interface, it would cause the rapid cooling of the molten. The atoms could happen the ordering transition by transfer movement in the cooling process and the transfer process require not only the energy but also the time. Once the cooling speed is too fast to form the crystalline state, the AP is metastable to generate. The freezing mainly occurs in the two interfaces, might produce either the crystalline or amorphous phase are all depended on the cooling speed. If the rate of atoms ordering keep up with the cooling speed, it would lead to the crystalline matter, if not, the amorphous phase. For the PEO, the transient temperature produced by plasma discharges is about 10000 K, the plasma discharge durations is as short as 10-100 µs in the "cascades" for Al and plasma discharge event rates is in the range of 10²-10³mm⁻²s⁻¹[36]. Since the extreme temperature difference in the two-phase interface and the short cooldown time with numerous plasma discharges, it is inevitable for the APs to generate. In addition, APs are metastable in contrast to their crystalline phases, and would transform into the crystalline phases when they are heated up to certain temperatures, so it is also possible that there exist amorphous-crystalline transitions in the process of PEO due to the instant high temperature.

The formations and transformations of CPs and APs would be complex, which are suggested as follows. The origination of γ -Al₂O₃ phase should be a direct PEO product or/and a crystallization phase of the amorphous phase, following equation (2) [37]:

$$Al_2O_3(AP \text{ or/and molten}) \rightarrow \gamma - Al_2O_3$$
 (2)

For mullite phase, Dr. Rachida found that the formation of mullite mainly depends on calcination temperature and the kinds of starting materials, and the silica, either amorphous or crystallized,

does not react with α -Al₂O₃ to form mullite [38]. All of materials that participate in the formation of mullite are γ -Al₂O₃ and silica. Moreover, the vast majority of silica in the PEO is deemed to be the amorphous phase, some of these thoughts are described later in this paper, the reaction mechanism is described in equation (3) [38]:

$$3\gamma - Al_2O_3 + 2SiO_2 (AP \text{ or/and molten}) \rightarrow 3Al_3O_2 \cdot 2SiO_2$$
 (3)

As for the α -Al₂O₃ phase (20=43.34° and 57.48°), it might originate from a direct PEO product or/and a crystallization phase of the amorphous phase or/and the transformation of γ -Al₂O₃ phase [36]. As far as is currently known, the production of α -Al₂O₃ could be described as shown in equation (4) and equation (5) [37, 39]:

$$Al_2O_3 (AP \text{ or/and molten}) \rightarrow \alpha - Al_2O_3$$
 (4)

$$\gamma - Al_2 O_3 \xrightarrow{1150^\circ \text{C} - 1200^\circ \text{C}} \alpha - Al_2 O_3 \tag{5}$$

The generations of isomers γ -Al₂O₃ and α -Al₂O₃ are related to the different cooling rate of molten alumina. The molten alumina will occur solidification and transform into γ -Al₂O₃ phase or/and even amorphous phase when the cooling rate is rapid. Otherwise, α -Al₂O₃ phase will be formed when the cooling rate is slow. Of course, the α -Al₂O₃ phase can also be transformed from the γ -Al₂O₃ phase when the latter is heated over the critical point, such as up to 1150-1200°C. 3.5. Distribution and crystallization behavior of amorphous phase in the coatings

The differential scanning calorimetry (DSC) test result of T-30 coating powders is shown in Fig. 5. In theory, the physical properties of AP would change because of the structural relaxation of phase equilibrium at higher temperatures, and when the temperature is heated to a certain degree, AP will transform into the CP, leading to evident crystallization peak(s) (exothermic) in the differential thermal analyzer, such as DSC[35]. But because of the complexity of phase compositions in the PEO coating, it has both CPs and APs (Fig. 4), its exothermic reactions are complicated. In order to investigate the phase transformation in the PEO process, further XRD

researches were carried out. Selected three points of the DSC curve, they are 1250K, 1400K and 1723K respectively. Except for the comparison group, the rest three powdery specimens were heated to the three temperatures, respectively. Then the specimens were cooled to the room temperature and performed the XRD experiments, the results are shown in Fig. 6. By contrasting sample (a) and sample (b) data, it is shown that the sample which had been heated to 1250K occur the diffraction peaks of γ -Al₂O₃ having an small increase in the X-ray diffraction. In addition, the height and range of AP peak of sample (a) are different from the sample (b). Initially the range of AP peak is between 13° and 40°, then its range becomes about 17°-30°, as is shown in the Fig. 6(II). It is known that the amorphous Al_2O_3 could be transformed into γ - Al_2O_3 when the temperature heated to about 900K[40], and the fundamental principle of quantitative analysis of XRD is the diffraction intensity of a phase is directly proportional to its content[41]. Hence, it can be inferred that the crystal transition of amorphous alumina would happen when the temperature is heated to 1250 K. By contrasting the XRD patterns of sample (b) and sample (c), it can be found that the diffraction intensity of AP does decrease, meanwhile, almost all of crystalline phase mullite increase in the intensity. Therefore, it can be deduced that the main exothermic peak is primarily concerned with the crystallization process of amorphous phase silica transform into the crystalline phase mullite, the formation mechanism is shown in formula (3). At last, by contrasting the curve of sample (c) and sample (d), two main obvious changes can be found. Firstly, there is a new crystalline phase-SiO₂. For silica, it is characterized by high amorphous formation ability. Specifically, AP could be generated even in the cooling rate of 10^{-3} K/s for the liquid silica[42]. In other words, the silica is hard to form crystalline phase, the higher temperatures are required for the AP to be transformed into CP. That's the reason why the crystalline phase silica is generated until the temperature is heated to 1723K. Secondly, the content of α -Al₂O₃ phase got more than ever and even a new diffraction peak of α -Al₂O₃ appeared

in about 2θ =43.34° of XRD spectrum and almost all of γ -Al₂O₃ peaks disappeared. That's because almost all of γ -Al₂O₃ phase could transform into α -Al₂O₃ phase when the temperature is heated up to about 1600K[43], the reaction equation is shown in formula (5).

In order to accurately analyze the content evolution of phase compositions of the coatings, the quantitative XRD results were obtained by using matrix-flushing method (number-K method), as shown in Fig. 7. The content of various phases are calculated by equation (6)[26, 44]:

$$X_{i} = \left(k_{f}/k_{i}\right) \cdot \left(I_{i}/I_{f}\right) \cdot X_{f}/(1 - X_{f})$$

$$\tag{6}$$

where X_i is the content of the coating phase composition to be examined, X_f is the mass percentage of the flushing material in the mixed powder (20%), k_f is the reference intensity of the flushing material, k_i is the reference intensity of the phase to be measured, I_f is the intensity of the strongest diffraction peak of the flushing material, I_i is the intensity of the strongest diffraction peak of the substance to be tested. By using the formula (6), the results of the phase compositions of powdery coatings that produced from four different time points are listed in Table 1. The results of Table 1 show that there mainly exist four kinds of phases in the coatings. i.e., mullite, γ -Al₂O₃, α -Al₂O₃, AP. It is obvious that the content of AP decreases and the total content of CPs increase with time. Meanwhile, it can be known that the change trend of the content of γ -Al₂O₃ phase, is not like those of mullite and α -Al₂O₃, does not increase but decreases, which verifies that a part of γ -Al₂O₃ phase was transformed into α -Al₂O₃ phase, or/and react with AP to form mullite phase. It is consistent with the preceding analysis results, the reaction processes are shown in formula (5) and (3), respectively. Secondly, there are evident differences on the content of AP among PEO powdery samples which taken at various treatment time points, but it could be sure that the total mass of both the CPs and APs increased with time by taking into account the thickness curve of the samples (Fig. 1).

Moreover, layer by layer XRD determinations were carried out in order to reveal the distribution rule of AP in the typical PEO coatings of T-30. The XRD patterns for the coatings of different levels of thickness-reduction are shown in Fig. 8. The XRD spectrum results indicated that the intensity of mullite showed a fairly noticeable decrease after the thickness-reduction treatment. It indicates that the closer to the C/E interface, as for sample T-30, the more content of mullite. This should be one reason for appearing the phenomenon of Si element enrichment in the EDS tests in the sample T-30, as is shown in Fig. 3. In order to study the distribution rule of APs and CPs, the direct comparison method is used to semi-quantitative calculate the relative content of phase composition in the coatings, as is shown in formula (7)[45, 46]:

$$X_{\alpha}/X_{y} \approx \left(I_{\alpha}/I_{y}\right) \cdot \left(k_{\alpha}/k_{y}\right) \tag{7}$$

where X_{α} and X_{y} are the content of α -Al₂O₃ and the phase to be examined, respectively. k_{α} and k_{y} are the reference intensity of α -Al₂O₃ and the phase to be examined, respectively. I_{α} and I_{y} are the integral intensity of α -Al₂O₃ and the phase to be examined (peak area, not peak height). Taking into account the main peak intensity of α -Al₂O₃ phase (20=57.48°) keeps a relatively small change in the different samples, it is assumed that the α -Al₂O₃ distributes uniformly in the coating, and the analysis results are shown in Table 2. Based on the data in Table 2, the content of AP of is calculated by formula (8):

$$AP(wt.\%) = \frac{X_{AP}/X_{\alpha}}{X_{AP}/X_{\alpha} + X_{mullite}/X_{\alpha} + X_{Y}/X_{\alpha} + 1}$$
(8)

The semi-quantitative content results of amorphous phases in the coatings with different thickness-reduction levels are shown in Table 3. It can be seen that the intensity of AP decreases significantly after the thickness-reduction treatment, which indicated that most of APs are existed in the outer layer of the PEO coatings. In our opinion, the distribution law of AP is closely related to the process. To be specific, in the beginning, the moment that have electricity, the surface of aluminum substrate would quickly form a dense oxide layer because of the strong affinity of

alumina. Generally, it is a very thin amorphous oxide films what is called "barrier layer" [47]. In the anodic oxidation stage, the oxide film is consist of AP. The increase thickness of oxide layer causes a dramatic increase in resistance. At the moment, the voltage presents an upward tendency in a straight line, as is shown in the phase I of Fig. 1. As the voltage continues to increase, the phenomenon of plasma spark discharge will emerge. The instant temperature of plasma discharge is extremely high, it will not only make the substrate where near the micro-arc area melts, but also make the liquid vaporizes and produce high air pressure[14, 36]. Soon afterwards, all kinds of ions from the electrolyte enter into the spark discharge reaction zones through the channels and have complex reactions with molten substrate. At the stage II, though the APs is still generated, a big part of products could be cooled sufficiently to form the CPs because the coatings already have a certain thickness [48]. At this stage, the morphologies of C/S and C/E interface could be seen in Fig. 2 (T-1 and T-2). At the stage III, the morphologies of C/S and C/E interface could be seen in the Fig. 2 (T-5, T-10 and T-15). At this stage, the APs may be relatively evenly distributed in the coating, and the phenomenon of silicon element enrichment is not obvious. At the stage IV, for the side of C/E interface, more APs generate due to the molten direct contact with the electrolyte, and the silica is included in APs. In addition, because the existence of "type A" discharge, there will be a portion of silicon elements enter into the C/E interface via the secondary reactions between alumina and amorphous phase silica, the reaction mechanism is shown in formula (3) (Section "B"in the Fig. 2). As a result, the difference of microstructure images and elemental composition between the C/E interface and C/S interface become more visible, as is shown in the Fig. 2 (T-20 and T-30). This should be another reason for the difference of elemental composition between C/E and C/S interface in the PEO coatings of middle and later stage.

Conclusions

The growth mechanism of PEO coatings is always a process of dynamic equilibrium which is affected by electrolysis conditions. All these conclusions mentioned by authors are based on the silicate alkalescent electrolyte at low constant current. But some same principles and analysis results also could be applied to other electrolytes and other valve metals. In the present study, the main four conclusions can be drawn as follows.

(I) There exists cracks and pores on the outer surface, it will become more obvious over time. With elongating treatment time and increasing the thickness of coating, the elemental composition of C/E interface becomes enriched in Si element. All the C/S interfaces have the aggregation morphology of hemispherical oxides, and the agglomeration bodies become larger over time.

(II) The aluminum and oxygen elements remain nearly unchanged for the sample of different treatment time points between the C/S interface and the C/E interface. But the silicon element have a tendency of enrichment from the C/S interface to the C/E interface in the sample T-30.

(III) The main phase compositions of PEO coatings are γ -Al2O3, α -Al2O3, mullite and amorphous phases. The amorphous phases in the PEO coatings are mainly alumina and silica.

(IV) With elongating the treatment time, the content of AP and γ -Al₂O₃ phases decrease, whereas the content of α -Al₂O₃ and mullite are opposite. The amorphous phases are mainly found in the outer layer of the coatings in the sample T-30.

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Figure captions

Fig. 1. The voltage-time curve with morphology evolution pictures of spark discharges and coating thickness-time curve during the PEO process.

Fig. 2. Morphologies of C/E and C/S interfaces and EDS results of different time points: (1), (2), (6), (7), (11), (12), (16), (17), (21), (22) (26), (27), (31), (32) are the morphologies of C/E interface. (4), (5), (9), (10), (14), (15), (19), (20), (24), (25), (29), (30), (33), (34) are the morphologies of C/S interface. (3) is a selected area EDS result from (2), (8) is a selected area

EDS result from (5), (13) is a selected area EDS result from (17), (18) is a selected area EDS result from (20), (23) is a selected area EDS result from (32), (28) is a selected area EDS result from (34).

Fig. 3. Cross-sectional microstructures and EDS mappings of the PEO coatings of T-5, T-10, T-20 and T-30.

Fig. 4. X-ray diffraction spectrum obtained from the PEO coating of T-30 without the substrate.

Fig. 5. Differential scanning calorimeter curve of the powdery coatings of T-30.

Fig. 6. XRD patterns for the powdery coatings under different heating temperatures: (a) powdery coating under no heating treatment; (b) 1250 K; (c) 1400 K; (d) 1723 K. (I) is the integrated figure, (II) is a partial enlarged view of curve (a) and (b), (III) is a partial enlarged view of curve (b) and (c).

Fig. 7. X-ray diffraction spectra patterns for powdery coatings under different PEO treatment time points: (a) 5min; (b) 10min; (c) 20min; (d) 30min.

Fig. 8. XRD patterns for the same PEO coatings of T-30 with different thickness-reduction values: (a) original thickness; (b) reduce the thickness to 20.5 μ m; (c) reduce the thickness to 12.6 μ m.

Table captions

Table 1 The specific content of phase compositions of powdery coatings obtained from different

 PEO treatment time points (wt. %).

 Table 2 The semi-quantitative relative content of phase compositions of PEO coatings with different thickness values.

 Table 3 The semi-quantitative content result of amorphous phases for the same PEO coatings

 with different thickness values.

Table 1

	Mullite	γ -Al ₂ O ₃	α -Al ₂ O ₃	Amorphous	MgO	
5 min	9.6	22.6	1.1	46.7	20	
10 min	19.0	13.6	3.1	44.3	20	
20 min	22.0	12.5	3.9	41.6	20	
30 min	32.5	11.0	4.9	31.6	20	

Table 2

	α/AP	α/mullite	α/γ
28.6 µm	1:10.1	1:9.1	1:3.8
20.5 µm	1:2.3	1:4.7	1:1.7
12.6 µm	1:0.2	1:3.5	1:1.6

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Table 3

Thickness (µm)	28.6	20.5	12.6
Content (wt. %)	42.1	23.7	3.2
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0			



Fig. 2.



Fig. 3.



Fig. 4.

















Fig. 8.







Highlights

The content evolution of phase compositions of Al-based detached PEO is measured.

The amorphous phases of Al-based PEO coatings is investigated by XRD and DSC.

The distribution rule of amorphous phases is studied by thickness-reduction method.

The formation and transformation of amorphous and crystalline phases is analyzed.