Preparation and Characterization of Amorphous Layer on Aluminum Alloy Formed by Plasma Electrolytic Deposition (PED)

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Abstract: In this investigation, protective layers were formed on aluminum substrate by Plasma Electrolytic Deposition (PED) using sodium silicate solution. The relation between the thickness of the layer and process time were studied. XRD, SEM, EDS were used to study the layer's structure, composition and micrograph. The results show that the deposited layers are amorphous and contain mainly oxygen, silicon, and aluminum. The possible formation mechanism of amorphous [Al-Si-O] layer was proposed: During discharge periods, Al_2O_3 phase of the passive film and SiO_3^{2-} near the substrate surface are sintered into $xSiO_2(1-x)Al_2O_3$ and then transformed into amorphous [Al-Si-O] phase.

Key words: plasma electrolytic deposition, amorphous layer, aluminum alloy

PLASMA Electrolytic Deposition (PED) is a relatively new technology to form ceramic layers on some non-ferrous metal and their alloys such as aluminum, magnesium and titanium[1,2]. By apply high electrical potential between the work-piece and another counter electrode in certain electrolysis, the breakdown of the passive film or the gas envelope surrounding the workpiece lead to electrical discharge in the interface between the workpiece surface and the electrolysis. Ceramic layers and/or diffusion layers are formed on the workpiece in such plasma-enhanced physical and chemical process.

If sodium silicate is added in the electrolyte, the formed layers may contain Si element. The layers are compound of Al_2O_3 and Al-Si-O phase with complex structure.[3]

As the temperature in the discharge channel is so high, the formed ceramic phase is welt and rapidly decreased to room temperature because of the cooling effect of the electrolysis. The process is non-equilibrium extremely and amorphous phase is formed in the layers[4]. On certain condition, the layers are amorphous entirely[5,6].

In this paper, [Al-Si-O] amorphous layer is formed on aluminum alloy in sodium silicate solution. The layers' structure, composition, and morphology are investigated by XRD, EDS, SEM. The possible mechanism for the forming of amorphous [Al-Si-O] layers is proposed.

1. Experimental

Al-4Cu-1Mg 2024 aluminum alloy plates in the size of 22×17×3 were used as the substrate materials, and aqueous solution of 80g/L sodium silicate was used as the electrolyte for PED. Before PED process, the samples were ground with 400# abrasive papers and cleaned with tap water. Amorphous layers were prepared with AC pulse PED equipment, which consisted of power supplier, signal detection and control system, a stainless steel container and cooling system. During the process, aluminum substrate is taken as anode while the stainless steel container is taken as cathode and the current density were fixed at 0.3mA/mm^2.The processed time were in 60 minutes.

The thickness of the layers was determined with eddy current thickness meter. The surface and cross section morphology were determined with scanning electron microscope (SEM). The structure and composition of the layer was analyzed by X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) on the cross-section. During SEM and EDS test, thin carbon films are sprayed on the sample to avoid the concentration of electrons as the PED layers are insulated.

2. Results And Discussion

2.1 Voltage between Two Electrodes

When a constant pulse current with average current density of $0.3mA/mm^2$ passed through the anodic sample, passive film was formed on the substrate. Because of the high electrical field near the interface between the substrate and electrolysis, the passive film or the gas envelope were broken down while new insulated phase were formed. While time elapsed, the changes of the electrode/electrolysis system about electrical parameters lead to the changes of average voltage between the two electrodes.

The average voltage between anode and cathode as a function of processed time is shown in fig.1. Because the electrical source is pulse mode, the peak voltage is higher than average voltage. During the PED process, the average voltage was lower than 105V, but the peak voltage was so high that the breakdown of the dielectric layer occurred in 2 minutes. At the beginning of the deposition, the voltage increased rapidly. After a certain time such as 15 minutes, the increase stopped and the average voltage between the two electrodes kept almost constant.

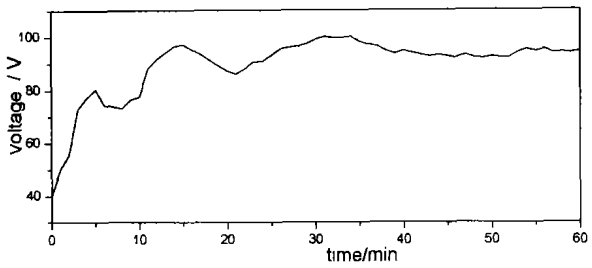

Fig. 1.Voltage between two electrodes

2.2 The Relation between the Layer's Thickness and Processed Time

The variety of the layers' thickness as a function of processed time is shown in Fig.2. It shows that the thickness of the layers increases when the processed time is increased, and the layer's thickness reaches at 74 μ m when the processed time is 60 minutes. By nonlinear fitting of the experimental dates, the relation between the layer's thickness and the processed time is given in the empirical formula $y = a \cdot x^b$.

Here y is the layer's thickness and x is the processed time, a and b are determined by experimental dates and varies with current density as well as composition and concentration of the solution. In the condition mentioned above, a and b are 5 and 0.64 respectively.

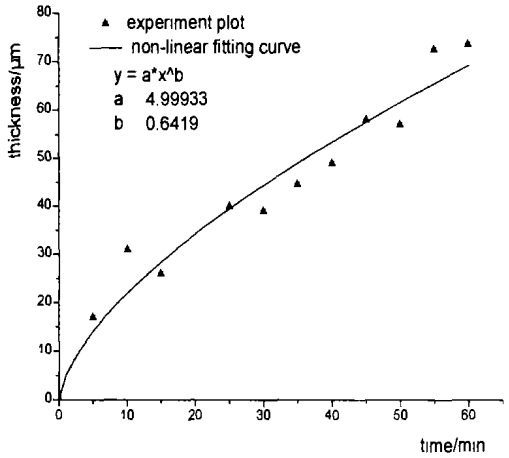

Fig.2 The relation between the thickness of the layers and process time

2.3 Micrograph of Cross Section and Surface

The surface and cross section micrograph of the sample processed 60 minutes are shown in fig.3. The layer is porous and the pores have a diameter from about 1 μm to 20 μm. The typical porous morphology shows the melt and solidification of the layer. The interface between the layer and substrate is obvious in the bottom of the cross section micrograph. A dense inner layer like other reports can not be observed in the cross section by SEM.

2.4 Structure and Composition

The result of XRD and EDS of the layer are shown in fig.4 and fig.5 respectively. In the X-Ray diffr-actogram, only the lines of Al substrate can be find and a big bulge appear near $2\theta = 22.38$. The bulge is not natural XRD peak. The result of XRD in fig.4 shows

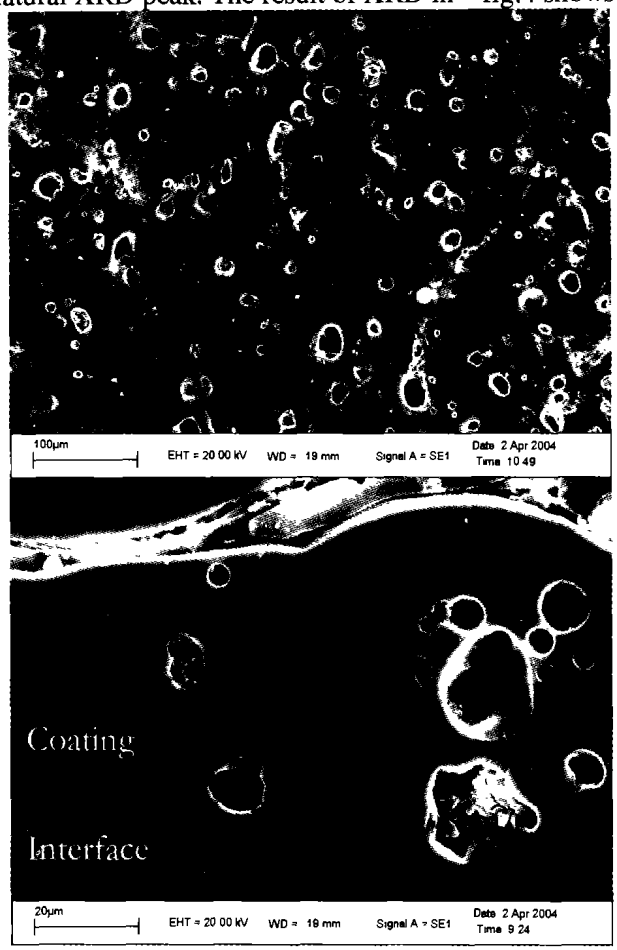

Fig.3. The surface and cross section morphology of the layer. (a): surface (b): cross section

that the layer is amorphous. EDS on the cross-section of the layer shows that the principal elements of the amorphous layer are oxygen, silicon, and aluminum. In addition, a little sodium element can be find. The atomic composition of these elements is shown in table 1. The contents of oxygen and silicon and aluminum in the amorphous layer are almost constant along the thickness and the former two elements decrease obviously at the interface, while the content of aluminum increases obviously at the interface.

$Al_{0.5}Si_{0.75}O_{2.25}$ (PDF number: 37-1460) has only one peak at $2\theta = 22.51$, combining XRD and EDS results, we suggest that the layer is amorphous Al-Si-O phase with a similar structure as $Al_{0.5}Si_{0.75}O_{2.25}$. The mechanism of the forming of amorphous Al-Si-O layer can be explained below.

While the current pass through the aluminum alloy substrate, Al_2O_3 passive film is formed on the substrate. Anions SiO_3^{2-} in the solution moves to the substrate surface by the action of electric field. When the breakdown of passive film or the gas envelope surrounding the workpiece occur, Al_2O_3 phase of the passive film and SiO_3^{2-} are sintered into $xSiO_2(1-x)Al_2O_3$ then into amorphous Al-Si-O phase.

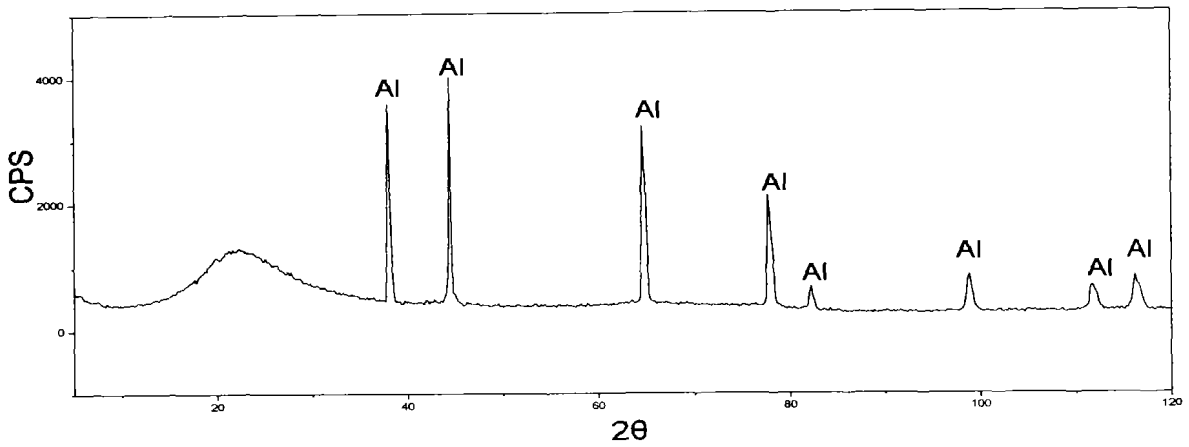

Fig.4. XRD result for the sample processed 60 minutes.

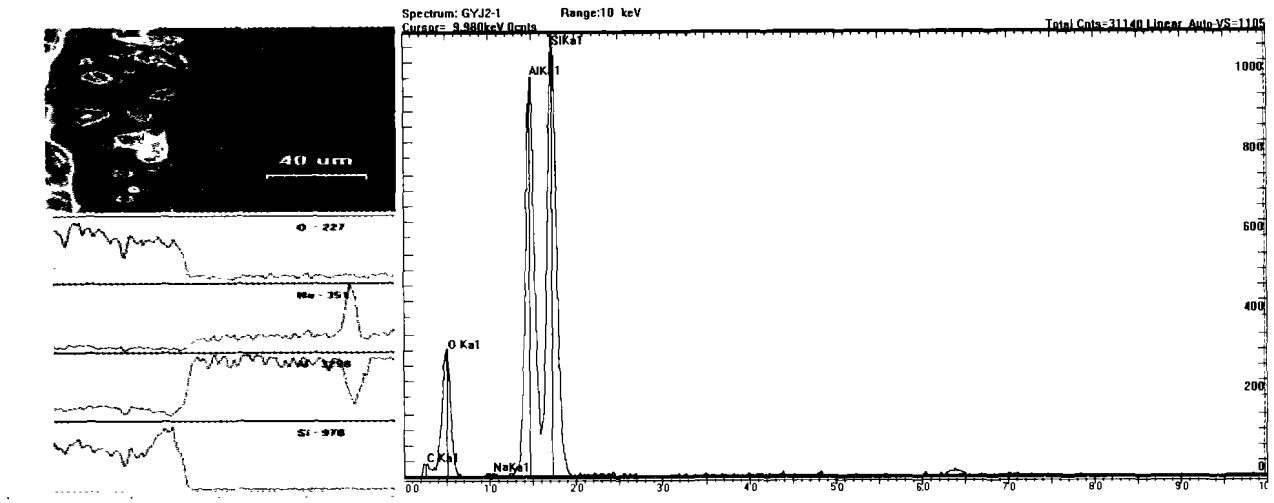

Fig. 5 Energy dispersive spectroscopy and elements distribution along the thickness

Table 1: The element composition of the layer (atomic%)

O	Si	Al	Na	Total
60.916	21.79	17.11	0.19	100

3. Conclusions

(1)Amorphous layer with thickness over 70 μm have been formed on aluminum alloy using sodium silicate solution. The average voltage between two electrode keeps at about 100V after 15min.The relation between the thickness of the layer and processed time is $\delta = 5t^{0.6}$.

(2)The layers are porous. XRD and EDS show that the layers are amorphous and contain mainly Al, Si and O.

(3)The possible mechanism of the form of amorphous Al-Si-O layer was proposed: During discharge periods, Al_2O_3 phase of the passive film and SiO_3^{2-} near the substrate surface are sintered into $xSiO_2(1-x)Al_2O_3$ then are transformed into amorphous Al-Si-O phase.

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