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Synergistic effect of rare earth salt and organic acid in the anodization of aluminum in phosphoric acid

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Abstract The effect of rare-earth element (cerium salt) and organic acid (citric acid) on the anodic oxide film obtained in phosphoric acid and their synergistic mechanism in the anodizing process were studied. The results show that the synergistic effect of cerium salt and citric acid in anodization of phosphoric acid can reduce surface defects, improve its microstructure and properties of the anodic oxide film. With the analysis of EDAX and XPS, the hydroxide of cerium salt was deposited on the film surface. It is deduced that cerium salt takes part in the formation of oxide film directly on the synergistic effect of citric acid.

Introduction

The anodization of aluminum in solutions such as sulfuric oxalic, chromic, and phosphoric acid have been extensively investigated in order to produce a coating which possesses excellent corrosion resistance and other commercially desirable qualities [1–4]. The aluminum anodic oxide film has been traditionally used for surface finishing. Recently, they also can be used as microfilters in aggressive environments [5] or as templates for the electrodeposition of metals and semiconductors [6, 7].

Rare earth elements have been used in many fields with strong chemical activities and rather large atomic radius. In recent years rare earth elements have been utilized in surface engineering such as chemical activities, flam spraying and electric plating [8]. Much work has been carried out on the investigation of the rare earth-based conversion coatings for aluminum alloys [9–12]. Recently, some researchers studied the application of rare earth on the aluminum anodization in sulfuric acid [13, 14]. However, some organic acid are always added into electrolyte in practical anodization to improve the properties of anodized film, and seldom work has been reported on the synergistic effect of rare earth and organic acid during anodization.

The present paper is intended to study the effects of cerium salt on the anodizing process and the anodic oxide films obtained in phosphoric acid-base solution, and provide an experimental basis so as to enlarge applications of rare earth elements.

Experimental

Annealed aluminum foils (99.99% purity, 3 mm × 3 mm × 0.5 mm) were used to grow anodic porous layers. High purity metal was preferred in order to minimize the influences of alloying elements. Prior to anodizing, the specimens were degreased and activated with sodium hydroxide at 60–70 °C for 3 min and then electropolished in a stirred alcohol and perchloric acid ($C_2H_5OH/HClO_4$) mixture for 3 min at 25 V, followed by ultrasonic rinsing in a cold distilled water for 5 min. An electrochemical reactor was designed and built to carry out anodizing experiments. Anodization process was conducted in a solution (4 wt% phosphoric acid) and b (a solution +0.05 wt% cerium salt +0.5 wt% citric acid, HC_it). The anodizing parameters: 12–13 °C, 1.0 A/dm^2, 30 min–1 h. After anodizing, each sample was washed thoroughly with distilled water and dried with an air jet.

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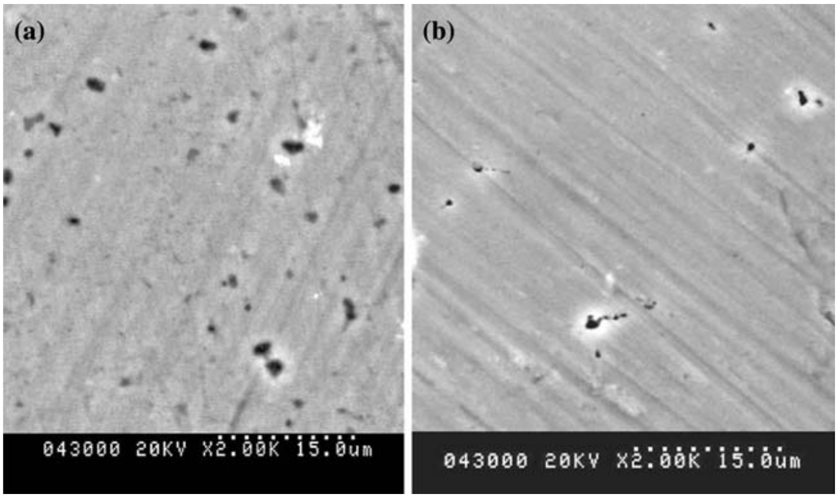

Fig. 1 Surface morphologies of the alumina layers. (**a**) phosphoric acid. (**b**) mixed solution 1.0 A/dm^2, 12–13 °C, 30 min

Film hardness was measured with HXD-1000 digital microhardness tester (load 50 g, loading time 15 s). Scanning electron microscopes (SEM, S-520 and JSM-6700F) and energy-dispersive analysis of X-rays (EDAX, CMIZ) were used to evaluate the effect of cerium salt on the microstructure of the anodic oxide surface. The chemical states of elements are examined by X-ray photoelectron spectrograph (XPS, PHI-5300/ESCA).

Results and discussion

Results

Effect of Re on the surface morphology

Figure 1 gives the surface SEM photographs of anodic oxide films in the traditional solution (a) and the mixed one (b). It can be observed that the sample surface is rough and exists a lot of big pores in defect in solution (a), while the surface defect reduces greatly with the addition of cerium salt. Furthermore, the surface becomes smooth (b).

Their further finer microstructures are shown in Fig. 2. In Fig. 2a, it clearly shows a disordered porous structure. The size and the shape of the pores are very irregular and some ellipsoidal pores with larger dimension are distributed along the rolling direction of the metal. This morphology further confirms that there are many defects exist on the surface of alumina obtained in solution (a) in which pores preferential nucleate. More regular pores are acquired in Fig. 2b. It indicates that the addition of cerium salt and organic acid better the microstructure of porous layers.

Effect of Re on the properties of film

Figures 3 and 4 give the thickness and hardness of film in different solutions after one-hour anodization. It can be seen that the addition of cerium salt and organic acid increases both the surface thickness and microhardness of porous

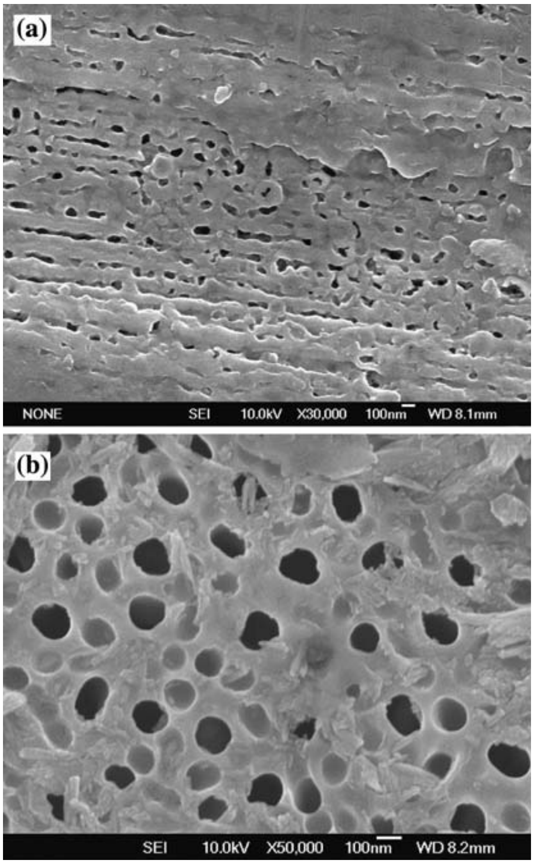

Fig. 2 FESEM pictures of the outer surface of porous alumina layers

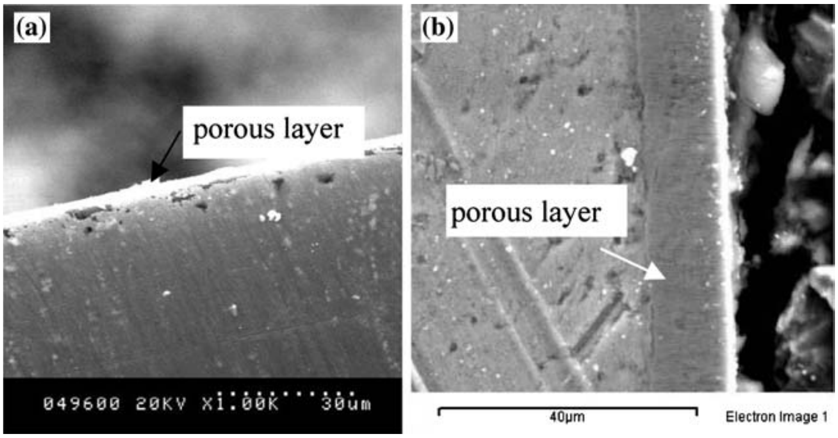

Fig. 3 Thickness of porous layers in different solutions

layers. The film thickens about 4 times, from 3 μm to 12 μm, and the hardness increases from 256 HV to 350 HV.

Synergistic mechanism

Z.L. Yang studied the effects of rare earth salts on the property of anodized films in sulfuric acid solutions. His result showed that rare earth salts could increase the thickness and hardness of the porous anodized films in a narrow range. He believed that rare earth salts were just as an accelerating agent during anodization because no content of the rare earth element was found in porous layers. However, in this experiment, cerium salt and organic acid plays an important role on the improvement of the structure and properties of porous layers in phosphoric acid, furthermore, some amount of cerium compound has deposited on the film surface (Fig. 5). Figure 6 gives the XPS spectra of Ce3d on surface. The analysis on the electron binding energy of Ce on the film surface indicates that this element exist in the form of Ce(OH). Therefore, in this mixed solution, Re salt is not just as an accelerating agent, but as a reactant to take part in the formation of oxide film directly on the synergistic effect of organic acid.

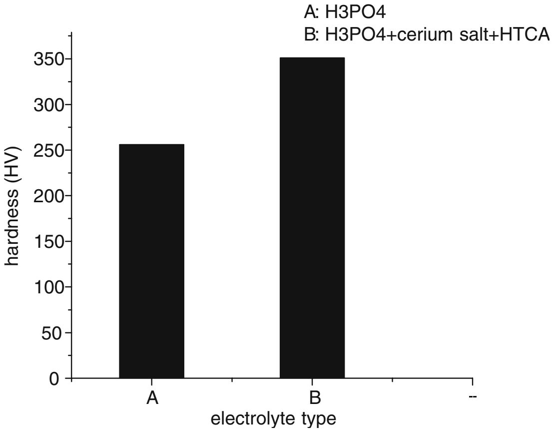

Fig. 4 Hardness of porous layers in different solutions

The experimental electrolyte is composed of phosphoric acid, organic acid and cerium salt. Oxygen atom has strong

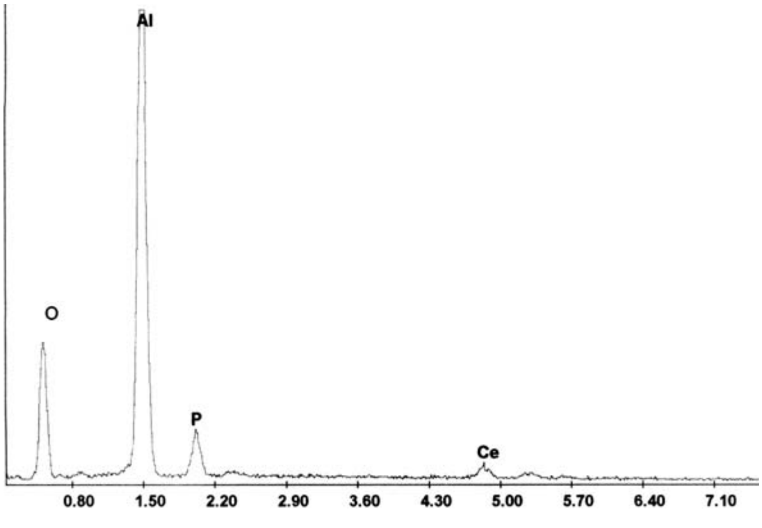

Fig. 5 EDAX spectra of the film surface

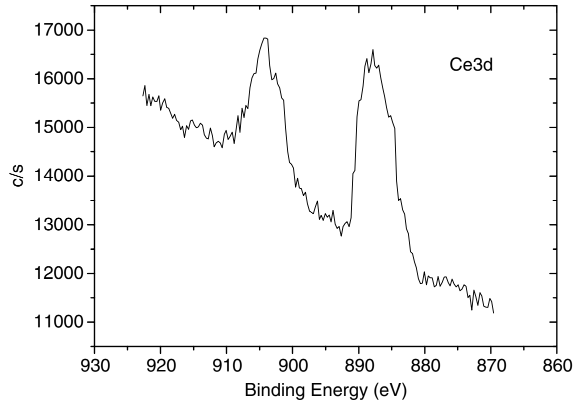

Fig. 6 XPS spectra of surface and Ce3d for anodic oxide film

coordinate power with rare earth ion, so rare earth ion is easy to bond with many ligands containing oxygen to form complex compounds [15]. The organic acid in this electrolyte is a kind of hydracrylic triprotic carboxylic acid which will act with Ce^{3+}as follows:

$$Ce^{3+} + HC_it \rightarrow \left[Ce(HC_it)_2\right]^-$$

Besides, Ce^{3+} would also act with excessive PO_4^{3-} to form a chelate complex in the solution:

$$Ce^{3+} + 2PO_4^{3-} \rightarrow \left[Ce(PO_4)_2\right]^{3-}$$

The action of cerium salt and citric acid in anodizing process can be concluded into two steps: one is their migration and adsorption to the anode surface (Fig. 7, I). During anodization, OH^-, O^{2-} and those oxy-acid ions migrate to aluminum surface (anode) on the power of electric field. Those ions with small ion radius can enter the oxide inner until reach the barrier layer. Those particle clusters, such as complex ions of rare earth and organic acid, mainly adherence on the outer surface because of their big size, especially prior to arise on the strong electrical field, such as those pore defects to make the electric field uniform, which can decrease the surface defects and the dissolving of the films by phosphoric acid.

The other step is the reaction and production of compound on the surface (Fig. 7, II). The pH value on anode increases with the migration and adsorption of OH^- on aluminum surface. Just as the cathode mechanics of rare earth conversion film [16], OH^- on the anode surface would lead to the deposition of Re ion.

$$Ce^{3+} + 3OH^- \rightarrow Ce(OH)_3 \downarrow$$

Besides, HTCA also can produce complex compound on the anode surface, which would remove H^+ from the surface to decrease the dissolving velocity of the films.

$$Al^{3+} + [HC_it]^{h-} \rightarrow Al(HTCA)_i;$$
$$Al(HC_it)^{i+}H^+ \rightarrow HC_it + Al^{3+}$$

Above all, the synergistical action of cerium salt and HTCA in anodization of phosphoric acid can reduce the film defects, decrease its dissolving velocity and produce hydroxide of rare earth on the surface, in result, the structure and properties of the film are improved.

Conclusion

In this work, the synergistic effect and mechanism of rare earth salt and HTCA on the aluminum anodization in phosphoric acid were studied.

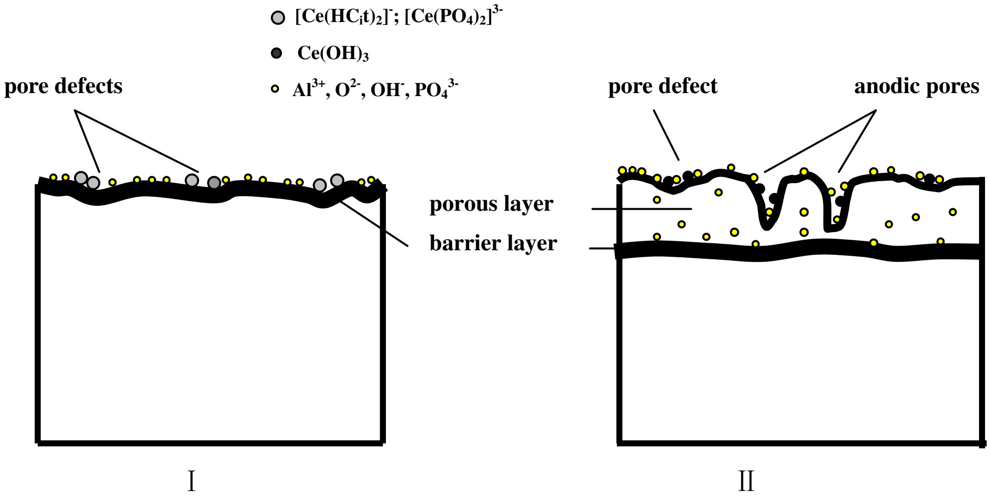

Fig. 7 The action of Re and HTCA in the anodizing process

The addition of cerium salt and HTCA affects the surface microstructure, composition, thickness and microhardness of anodic oxide film. These two additives can decrease surface defects to obtain better film; make the anodic pores more regular; change the element composition on the surface of oxide film and enhance film thickness and microhardness: the film thickens 4 times and hardens by 94 HV compared with the traditional one.

The synergistic mechanism of cerium salt and HTCA was also deduced. In the anodizing process of phosphoric acid, cerium salt and HTCA all take part in the formation of anodic oxide film. When anodizing, heir complex ions migrated and adsorbed on aluminum surface, especially those surface defects, to remove H^+ and produce Ce hydroxide deposited on the surface.

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