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Preparation and analysis of films on aluminium by high voltage anodization in phosphoric acid and sodium tungstate solution

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Abstract

A high voltage anodic film on aluminium was prepared in a mixed electrolyte of phosphoric acid and sodium tungstate. The properties, structure, morphology and chemical composition of the film were investigated. It was found that the elements in the film were O, Al, P and W and the main chemical compositions of the film were aluminium oxides with some phosphates and tungstates. Compared with conventional anodic films, the high voltage anodic film showed good hardness and excellent corrosion and heat resistance. Scanning electron microscopy indicated that the film could be divided into two layers, a porous surface layer and a compact underlayer. Many cracks were observed in both layers, which are significantly different from those of conventional anodic films.

1. Introduction

It is well known that two types of anodic oxide films on aluminium can be distinguished: the barrier film and the porous film with a thin barrier underlayer. The latter double-layer structure is typical for films obtained in electrolytes such as sulfuric acid, oxalic acid etc. [1]. Many models have been used to study the characteristics of these films [1–5]. The Keller model, which consists of a dense barrier layer adjacent to the substrate, followed by a film of densely packed oxide cells with one pore in the middle of each cell, is widely accepted [2]. The operating voltage for conventional anodization is in the range 30–120 V. Anodization under higher voltages was not investigated until Lasser et al. studied the high voltage anodization (HVA) of aluminium in oxalic acid in 1970 [5]. Brown et al. prepared ceramic coatings on aluminium by anodic spark deposition in aluminate and silicate solutions [6]. Xue et al. studied the ceramic coating on LY12 aluminium alloy formed by microarc oxidation in 5 g dm^{-3} NaOH solution [7]. Dong et al. studied the porous structure of alumina films formed by high voltage anodizing in chromic acid [8]. However, the work was not continued and little literature on HVA films on aluminium can be found.

Recently, HVA films on aluminium have been prepared in a mixed electrolyte of phosphoric acid and sodium tungstate [9]. In this work, the properties, structure, morphology and elemental composition of the HVA film are investigated. It is shown that HVA films on aluminium are different from conventional anodic films in many aspects.

2. Experimental details

Aluminium foil (thickness, 1.0 mm, purity; 99.5 wt %) was used as the specimen. The cathode was a stainless steel sheet of large area and the anode was a piece of aluminium sheet of dimensions 25 mm × 25 mm. The electrolyte was cooled with water and agitated with air.

Before anodization, the specimen was degreased and activated with sodium hydroxide (50 g dm^{-3}) at 60–70 °C for 3 min. To avoid oxidation of the wire, it was installed in a Teflon sleeve. The anodization was carried out at 35 °C in mixed electrolyte of phosphoric acid (6 g dm^{-3}) and sodium tungstate (3 g dm^{-3}) under constant voltage for 5 min. The voltage was adjusted to 225 V linearly within 30 s and then maintained stable until the anodization was over. The anode was then taken out, washed and dried in air. The baths were prepared with deionized water.

The hardness and thickness of the obtained films were measured with a Vickers hardness tester (HX-1000) and a Votex thickness gauge (7503), respectively. The stability of HVA films in acid and alkali was examined according to a known method [10] and JISH 8681-1976. The elemental analysis of the film were carried out by X-ray photoelectron spectroscopy (XPS-Las 3000, Riber). The structure and morphology were investigated by X-ray diffraction (XRD-D5000, Siemens) and scanning electron microscopy (SEM-JSM 5600 LV), respectively.

3. Results and discussion

3.1. *Characteristics of HVA*

HVA of aluminium in the mixed electrolyte features a high current density, high formation speed, low electrolyte concentration and wide operating temperature range. The total electrolyte concentration of phosphoric acid (6 g dm^{-3}) and sodium tungstate (3 g dm^{-3}) is much lower than that for conventional anodization systems. The dependence of current on time in the mixed electrolyte is shown in Figure 1. The peak current and its rate of decline are different from that for conventional anodization in sulfuric acid. In the case of conventional anodization, the maximum current, which is less than 5 A dm^{-2}, falls slightly with time and then increases to a steady value [1]. In HVA, however, the peak current reaches 32 A dm^{-2} under the present conditions, and is six times larger than that for conventional anodization. There is then a sharp decrease in current and no increase in current is noticed. This results in modifications in the formation rate of the film, which is shown in Figure 2.

According to Figure 2, the aluminum surface is covered with HVA film in 5 min. The thickness of the film is about 26 μm and the average formation rate is about 5 μm min^{-1}. No linear film growth behaviour was observed. Initially (AB, ~1 min), no obvious growth of the film was observed. In the second stage (BC, ~2 min), the film grows quickly with a rate of 10–12 μm min^{-1}. Finally, the growth rate slows down gradually. This means that the formation of HVA films occurs mainly in the second stage and the growth rate is much higher than that for conventional anodization.

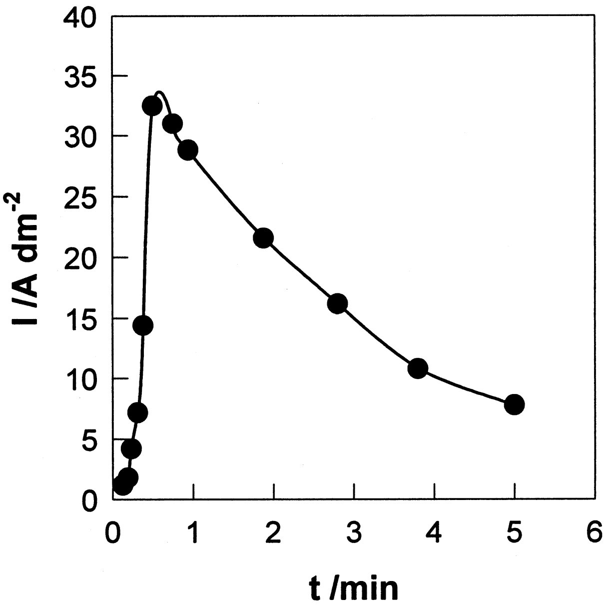

Fig. 1. Dependence of current on time during the HVA process of aluminium in the mixed electrolyte.

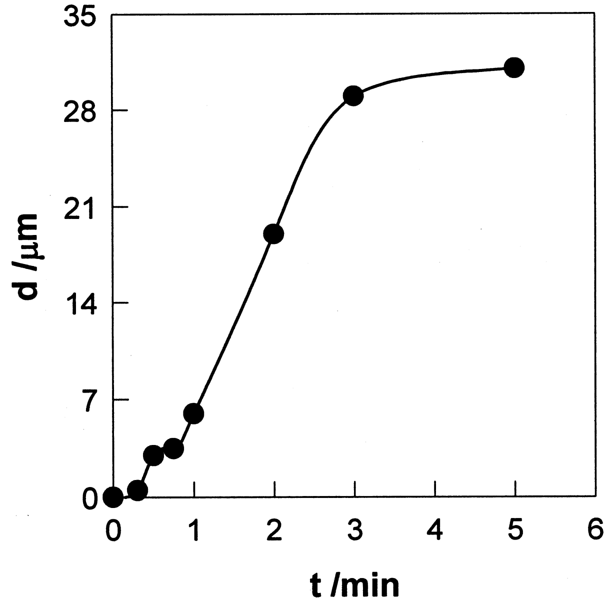

Fig. 2. Dependence of thickness on time during the HVA process of aluminium in the mixed electrolyte.

HVA can occur over a large temperature range (10–70 °C) and a very short time (5 min). This is of great advantage to application in industry. Usually, conventional anodization is operated at lower temperature and current density, and cooling equipment and long times are required, resulting in high consumption.

3.2. *Properties of the HVA films*

The hardness of the obtained HVA films was measured with a Vickers hardness tester (HX-1000). The hardness of HVA film is about 519 HV and is comparable to that of a hard anodization film. The chemical stability of HVA films was investigated by immersing the films into 36% (w/w) hydrochloric acid and 10% (w/w) sodium hydroxide aqueous solutions for 24 h. The film is very stable and cannot be dissolved. The chemical stability of HVA film is different from that of the conventional anodization film and may result from the different structure and composition of the HVA film. However, the aluminium substrate under HVA film is corroded in hydrochloric acid or sodium hydroxide aqueous solution. This means HVA film is porous, the corrosive solution can penetrate the film and then corrode the substrate. If treatment is adopted to seal the cracks and pores in HVA film, the protection ability of the film will be increased.

3.3. *Elemental composition and structure of HVA film*

Table 1 shows the XPS results of the elemental composition in HVA films. O and Al are the major composing

Table 1. XPS results of the elemental composition of HVA film at the different sputtering time

Sputtering time/min	O /at %	Al /at %	P /at %	W /at %
0	75.1	17.0	5.2	0.7
45	74.6	19.2	3.4	–
90	62.5	21.6	3.9	–

elements, but P and W are the minor ones. P and W may come from the incorporation of the electrolytic species. With increase in sputtering time, the elemental distribution of HVA film is changed, Al increases, but O, P and W decrease. The elemental distribution of Al and O is in agreement with that of the conventional anodic films. Table 2 also suggests that W only stays in the surface layer of the film and P exists in the whole of the film. Further analysis on the electron binding energy of the component elements was carried out. The binding energy of O and Al is related to the aluminum oxides, but P and W exist in the form of phosphates and tungstates, respectively. Therefore, the chemical composition of the film may be described as $Al_2O_3 \cdot mP_2O_5 \cdot nWO_3 \cdot xH_2O$ $(m, n \ll 1)$.

The X-ray diffraction pattern of HVA film is shown in Figure 3. It is the typical pattern of a non-crystalline structure. To investigate the thermal stability of HVA film, the film was annealed at 500 °C for 5 h and then XRD examination was carried out again. No noticeable change of XRD pattern was observed. This means HVA film has a good thermal stability and no structural change occurs at a temperature as high as 500 °C.

3.4. *Morphology of HVA film*

Figure 4 is the surface micrograph of HVA film. A porous surface can be observed and is similar to that of the conventional anodic ones. However, the pore size (0.1 μm) is 10 times larger but the porosity (10 μm^{-2}) is 100 times lower than that of conventional anodic films. This may result in superior properties such as hardness and corrosion protection [1].

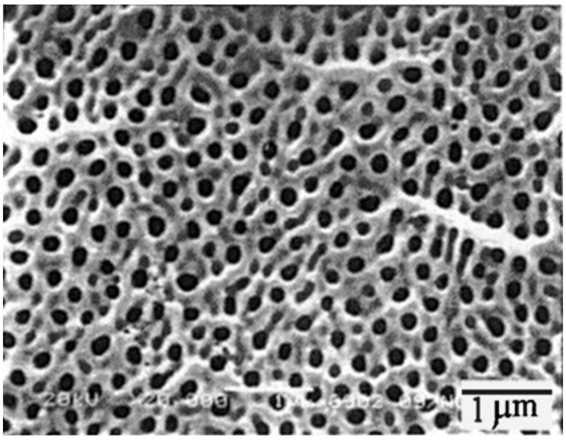

Fig. 4. SEM image of the surface micrograph of HVA film.

The cross-section micrographs of HVA films are shown in Figure 5. As observed in conventional anodic films, HVA film can be divided into porous and compact layers (Figure 5(a)). However, the difference is that many gas cavities exist in the porous layer of HVA film. Figure 5(b) shows the interface between the film and substrate. The film connects with the substrate in a jagged and interlocking pattern, which gives HVA film good adherence strength. In both porous and compact layers, a multicrack structure can be observed. A typical structure is shown in Figure 5(c). This structure differs greatly from that of conventional anodic films, and may result from a process of dehydration under high temperature during formation.

3.5. *Formation mechanism of HVA film*

According to the work of McNeil and Gruss [11], the growth of anodic films on aluminium in phosphate or tungstate solution may be divided into two steps: (i) the accumulation and precipitation of anions near the

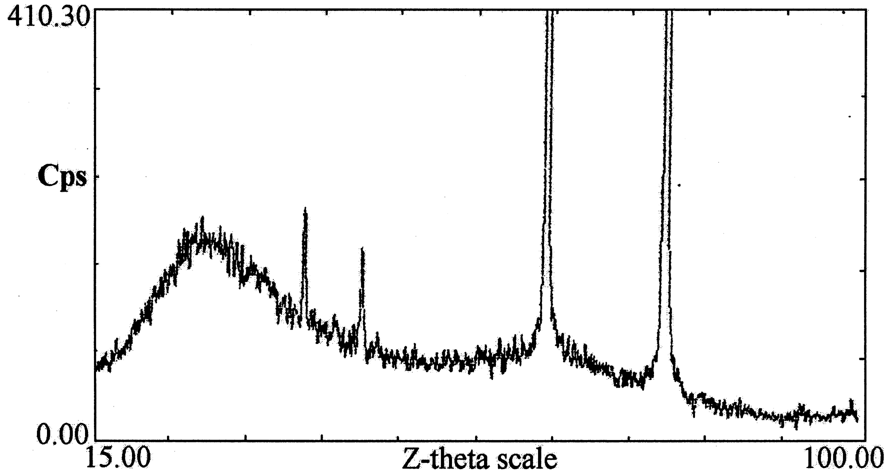

Fig. 3. XRD pattern of HVA film.

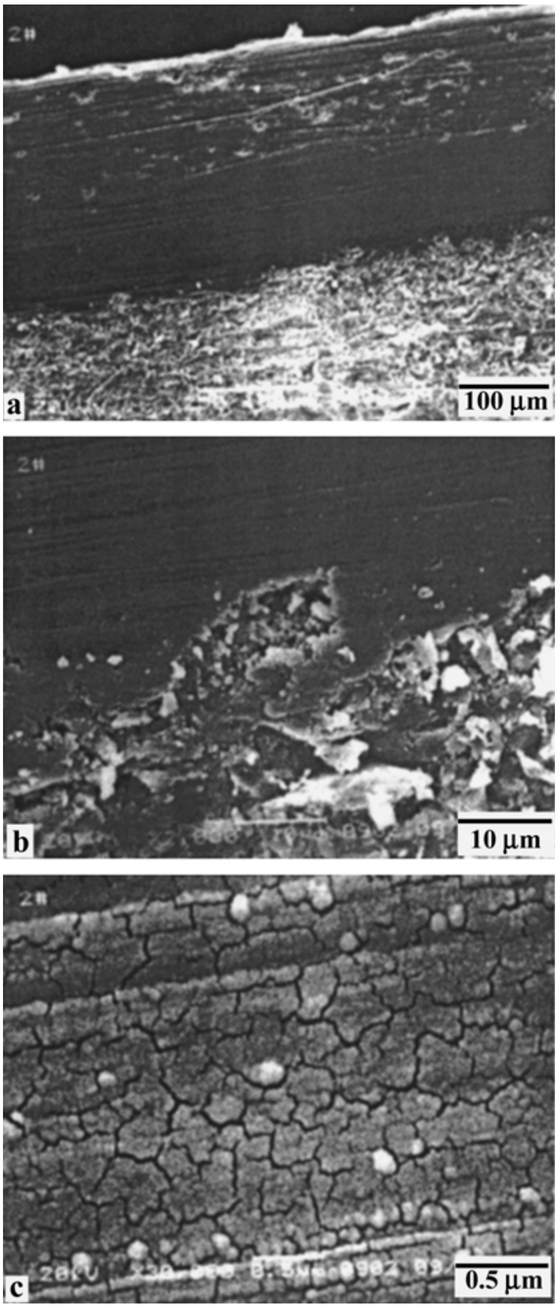

Fig. 5. SEM image of the cross-section micrograph of HVA film.

surface of the anode; (ii) the dehydration and crystallization of the deposited film. Skeldon et al. also pointed out that gels or precipitates were possibly formed in the anodization of aluminium in electrolytes such as tungstate and silicates [12]. Although these results were obtained in the case of low voltage anodization, they may also apply at the beginning of HVA. During the HVA process, a layer of gels or precipitates is formed due to the existence of WO_4^{2-} and the low pH in the interfacial layer between aluminium and solution. This gel layer acts as a surface barrier and results in a high cell voltage. With increase in the voltage, the current increases and the anode dissolves fast. Because the Al^{3+} migration to the electrolyte solution under the anodization field is prohibited by the surface barrier (gel layer), the Al^{3+} concentrates in the thin layer between the anodic surface and the gel layer and becomes super-saturated. At the same time, heat is produced by the high current density and the interfacial temperature may be very high. The super-saturated Al^{3+} may react with water, or PO_4^{3-}, to form aluminium hydroxide and phosphate. On the other hand, as Skeldon et al. suggested [12], the released H^+ migrates out of the thin layer and reacts with WO_4^{2-} to reinforce the gel. Under these electrochemical and thermal effects, the hydroxides, phosphates and gels may be transformed to HVA film by a process of melting, dehydration and condensation. The schematic illustration of the total process is shown in Figure 6. The growth rate of HVA film is higher than that of conventional film and some specific features, such as cracks, are observed in the cross-section micrograph. The current, which results in Al^{3+} and heat, decreases gradually with the formation of the film. When the concentration of Al^{3+} cannot reach the super-saturated state and the heat is insufficient to melt the composite oxides, the growth of HVA film ceases. Other side reactions, such as oxygen evolution, may replace the formation of HVA film.

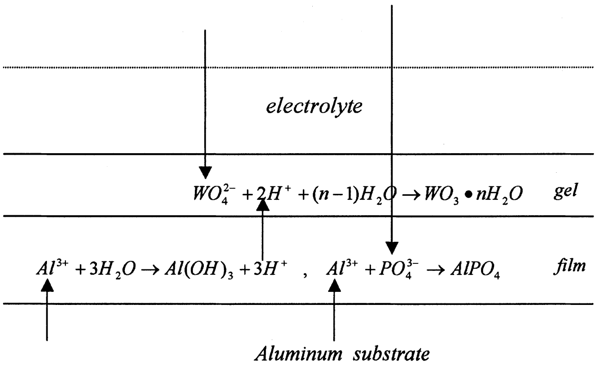

Fig. 6. Schematic illustration of the possible processes during the formation of HVA films.

4. Conclusion

High voltage anodization (HVA) films on aluminum were prepared in mixed electrolyte of phosphoric acid and sodium tungstate. The properties, structure, morphology and chemical composition of the obtained film were investigated. Compared with conventional anodic films, the film shows good hardness and excellent thermal and chemical stability. The elemental components of HVA film are O, Al, P and W. Aluminium oxides, together with some phosphates and tungstates, may be the main components in the film. The structure of HVA film is noncrystalline and can be divided into porous and compact layers. Many cracks are observed in both porous and compact layers and may result from dehydration of the film under high temperatures.

Acknowledgements

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