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Effects of alloying elements on microstructure and protective properties of Al_2O_3 coatings formed on aluminum alloy substrates by plasma electrolysis

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ABSTRACT

Hard alumina coatings were formed on three typical Al alloys using a plasma electrolytic oxidation (PEO) process. The microstructure and protective behavior of the coatings were characterized in the context of the elements alloyed in the substrates. The substrates investigated were three commercial aluminum alloys (Al 6061, 2024, 7075) and various Al – x–Mg binary alloys with $x = 0.6$–4.6 wt.%. The major portion of all coating films consisted of a mixture of γ- and α-alumina on top of a very thin amorphous substrate-based layer. Examination of the coatings on the commercial alloys reveals that the ratio of α- to γ-alumina is inversely proportional to the total concentration of residual Mg, Cu, and Zn ions in the coatings. Additional experiments on Al – x–Mg binary alloy substrates suggest that Mg ions play the most important role in suppressing the transition of γ- to α-alumina. Our results suggest that Mg content ≥ 3 wt.% yields only the γ-alumina. We propose a mechanism that correlates the residual elements in the coatings to the alumina phase transition. A higher content of the dense α-alumina in the coatings yielded greater hardness as well as improved wear tolerance and crack resistance of the coating layers.

1. Introduction

The plasma electrolytic oxidation (PEO) process is one of several techniques for fabricating thick metal-oxide coatings on lightweight materials such as aluminum, titanium, and magnesium. The technique involves anodic oxidation of the metal surface in an aqueous electrolytic solution together with localized plasma discharge, which occurs when the electrolytic voltage exceeds the critical polarization potential of the metals [1–4]. Previous studies have shown that such coatings, particularly alumina coatings, exhibit extremely high hardness and wear resistance as compared to coatings fabricated using conventional anodizing processes [5,6]. The excellent properties of alumina coatings are attributed to the phase transition from amorphous alumina to γ-alumina, and further, to extremely hard α-alumina. The heat generated by the plasma discharge in the oxide causes such phase transitions [7]. In the early stage of coating formation, discharged oxide layers are cooled so rapidly due to their small thickness that the γ→α transition does not occur. As film thickness increases, thermal dissipation in the coating is retarded and the transition from less dense phases to harder α-alumina becomes more prominent [7]. The selection of electrolytes and power sources is crucial for the resulting phases and coating structures. The details of these processing parameters have recently been presented and reviewed by Yerokhin [5].

In addition to these parameters, the alloy composition of the substrates can influence the coating properties. Some authors have reported that copper-containing aluminum substrates exhibit a higher content of α-alumina than magnesium-containing alloy substrates [1,8]. However, despite intensive studies using several aluminum substrates (such as Al 7075 [9], 2024 [10], 6082 [11,12], and Al–Zn–Mg [3] alloys), no systematic studies on the correlation between the substrate alloying elements and coating properties have been presented to date. Furthermore, a direct comparison of the reported data from different sources is not feasible due to differences in the processing parameters used for each case. The aim of the present study is to elucidate the role of major alloying elements in aluminum alloy substrates in determining the microstructure and protective properties of PEO coatings.

2. Experimental details

The substrate materials selected for this study were three commercial aluminum alloys (Al 2024, 6061, and 7075) and two binary Al – x–Mg ($x = 0.6$, 1.2, 3.0, and 4.6 wt.%) alloy systems. As shown in Table 1, the commercial 2024, 6061, and 7075 alloys are

Table 1
Chemical compositions of the aluminum alloy substrates.

Alloys	Heat treatment	Mg	Cu	Si	Zn	Mn	Cr
Al 2024	T6	1.56	4.40	–	–	0.62	–
Al 6061	T6	0.92	0.15	0.60	–	0.28	0.20
Al 7075	T6	2.49	1.35	0.18	5.11	0.14	0.20

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Table 2
Residual alloying elements (wt.%) in coated layers.

Alloys	Mg	Cu	Zn
Al 2024	0.53 (1.56)	0.44 (4.40)	–
Al 6061	— (0.92)	–	–
Al 7075	0.81 (2.49)	–	0.99 (5.11)

The values in parentheses represent chemical compositions in alloy substrates.

typical copper-, magnesium-, and zinc-containing alloys, respectively. The magnesium content in the three alloys is ordered as follows: 6061 < 2024 < 7075. The binary $\text{Al}-x$–Mg alloy systems were prepared to examine the effects of the Mg element separately. The ingot alloys were homogenized at 470 °C for 42 h and machined in the form of discs with dimensions $\phi30 \times t8$ mm and then immersed in a 10 L glass tank filled with an electrolyte. Amplitude-modulated AC with a constant current density (20 A/dm^2) was applied for 1 h, and the temperature of the electrolyte was maintained below 30 °C throughout the process. The electrolyte was a dilute aqueous solution of 3 g/L of KOH and 4 g/L of Na_2SiO_4.

Microstructural studies were carried out using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), and X-ray diffractometry (XRD). Chemical composition was analyzed by SEM-EDS on cross-sections of the coating layer. The measurements were performed at 5 μm intervals in a plane perpendicular to the coating. The chemical compositions shown in Table 2 are the average values of the measurements. The cross-sectional samples for TEM observations were prepared using a focused ion beam (FIB) system. For the XRD analysis and porosity measurements of the coating layer alone, oxide coating films were separated from the metal substrates by immersing each coated substrate in a saturated solution of NaOH. The pore size distribution of the free-standing coatings was measured by mercury intrusion porosimetry. Detailed procedures have been reported elsewhere [11]. The wear resistance was evaluated by carrying out a ball-on-disc sliding wear test using a SiC ball of 10-mm diameter. The

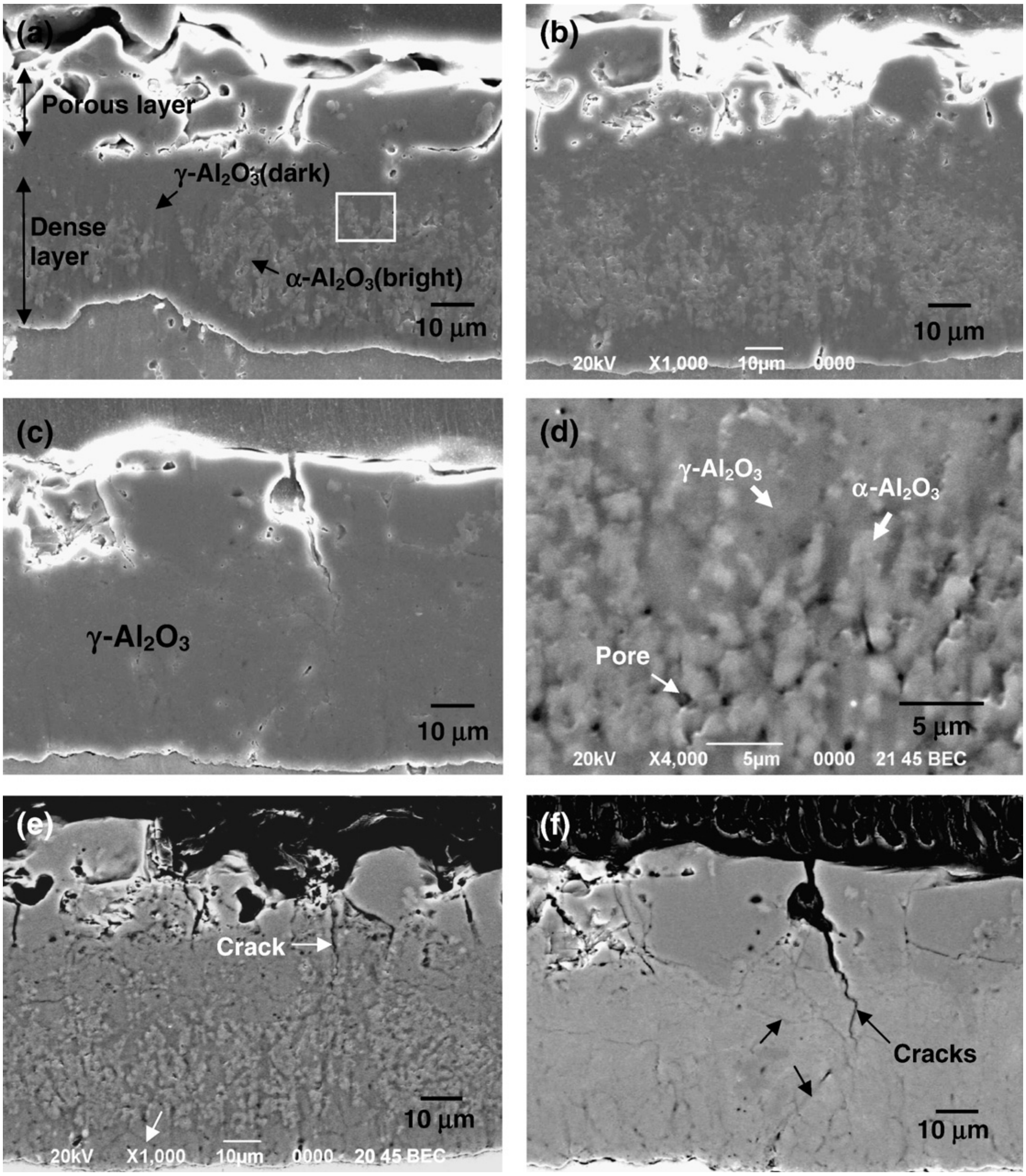

Fig. 1. Cross-sectional images of alumina coatings on (a, d) Al 2024, (b, e) Al 6061, and (c, f) Al 7075 alloy substrates. Panel (d) is a backscattered electron (BSE) image at the rectangular location on (a). Panels (e) and (f) are the BSE images of (b) and (c) at the same magnification, respectively.