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Growth of barrier-type anodic films on magnesium in ethylene glycol electrolytes containing fluoride and water

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ABSTRACT

This study demonstrates the formation of uniform barrier-type anodic films on magnetron-sputtered magnesium films at high current efficiency in ethylene glycol electrolytes containing 0.1 mol dm^{-3} NH_4F and various concentrations (0.1–28 mol dm^{-3}) of H_2O. The anodic films containing a crystalline MgF_2 phase develop both at the metal/film and film/electrolyte interfaces due to simultaneous migrations of anions inwards and cations outwards, respectively. When a Mg −1.2 at% Au/Mg bilayer film is anodized, initial prior oxidation of magnesium proceeds with gold atoms accumulating in a thin layer beneath the anodic film. The accumulated gold atoms are incorporated into the anodic film as a band when the alloy layer is completely anodized. Fluoride-containing gold species are formed by the incorporation and the gold species migrate outwards at a rate of 0.4 times the rate of Mg^{2+} ions. The addition of phosphate in the electrolyte results in the formation of an amorphous anodic film, and the phosphate incorporated into the anodic film is distributed throughout the film thickness. The transport number of cations is also influenced by the phosphate incorporation.

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1. Introduction

Barrier-type anodic films are formed on valve metals, such as aluminum, niobium, tantalum, titanium, tungsten and zirconium, in appropriate aqueous electrolytes at high current efficiency [1]. Because of the fundamental interest as well as practical importance, the growth of the barrier-type anodic films on these metals has been studied extensively. The anodic films formed on aluminum, niobium, tantalum and tungsten metals are usually amorphous, developing both at the metal/film and film/electrolyte interfaces by inward migration of anions and outward migration of cations, respectively. The transport number of cations during film growth is dependent upon the oxide composition and electric field [1–3]. The relatively high contribution of both cations and anions to ionic current is characteristic of the amorphous anodic oxides. The anodic films are contaminated with electrolyte anion species, and their distributions in the anodic films are also dependent upon their mobilities. Thus, the incorporated anions are often used as a tracer for the investigation of ionic transport process during film growth [4–10].

Compared with the above-mentioned metals, the growth of anodic films on magnesium is not well understood, despite their practical importance for corrosion protection and wear resistance [11], because of the difficulty of the formation of uniform anodic films on magnesium and its alloys at high current efficiency. This may be due to low chemical stability of anodic films on magnesium and/or the Pilling–Bedworth ratio for MgO/Mg of less than unity [12,13]. In anodizing of magnesium and its alloys, including industrially used Dow17 and HAE processes, chromium oxide and fluoride-containing electrolytes are often used [14–16], showing improved chemical stability of the anodic films, although these electrolytes have harmful effects on environments. Ono et al. reported the formation of a barrier-type film or a semi-barrier film in alkaline fluoride electrolyte except at around 5 V and breakdown potentials, where a porous film is developed [17].

Recently, fluoride-containing organic electrolytes have been utilized to form self-organized nanotubular and nanoporous anodic films on titanium [18,19], zirconium [20,21], niobium [22], tantalum [23] iron [24–26] and stainless steel [27]. The use of organic electrolytes enables the formation of thick porous anodic

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films on iron and stainless steel, and improves the uniformity of the self-ordered pore or nanotubular array as well as the thickening of the anodic films on valve metals. Understanding the behavior of metals in organic electrolytes is also of importance because organic electrolytes are widely used in lithium ion batteries and electric double layer capacitors.

However, only few studies have been conducted on anodizing of magnesium in organic electrolytes. Brunner et al. reported the formation of black porous anodic layers in water-free methanol or ethanol electrolytes [28]. The formation of barrier layers was reported by Asoh and Ono [29]. They used trimetylamine-containing ethylene glycol (EG) electrolytes with 10–40% water. The concentration of water influenced largely the growth behavior of the anodic films. Turhan et al. formed self-ordered magnesium oxy-fluoride nanoporous/tubular layers on WE43 magnesium alloy in HF-containing EG electrolyte [30]. The present authors have reported recently the efficient growth of the barrier-type anodic films on sputter-deposited magnesium in EG electrolyte containing NH_4F and H_2O [31]. Similarly, a barrier-type anodic film is formed at high efficiency on ZE41 magnesium alloy in glycerol electrolyte containing NH_4F and H_2O [32]. The efficient growth of the anodic films allows us to examine the ionic transport process in growing anodic films on magnesium in detail.

In the present study, anodic films have been formed on magnetron-sputtered magnesium in the fluoride-containing ethylene glycol electrolytes with various water concentrations to know the electrolyte compositions for efficient film growth. For a better understanding of the ionic transport processes, gold and phosphate tracers are introduced into the substrate and electrolyte, respectively. The resultant anodic films were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Rutherford backscattering spectroscopy (RBS). The electrochemical impedance spectroscopy was also used for examination of electric properties of the anodic films.

2. Experimental

Thin magnesium films of ~300 nm thickness were magnetron-sputtered onto glass or flat, anodized aluminum substrates using a 99.9% magnesium target of 100 mm in diameter. After evacuating the chamber to less than 5×10^{-5} Pa, DC magnetron-sputtering was performed at 0.5 A and 300 V for 3 min. For deposition of a Mg −1.2 at% Au film (~45 nm) superimposed on a Mg film, a 1 cm-square gold sheet was placed on the erosion region of the 99.9% pure magnesium target.

The deposited specimens were anodized at a constant current density of 10 A m^{-2} in EG electrolytes containing 0.1 mol dm^{-3} NH_4F and various concentration of H_2O at 293 K to selected potentials. An aqueous electrolyte containing 0.1 mol dm^{-3} NH_4F was also used. To introduce a phosphate tracer in the growing anodic films, 0.1 mol dm^{-3} K_2HPO_4 was added to the EG electrolyte containing 0.1 mol dm^{-3} NH_4F and 0.1 mol dm^{-3} H_2O. Anodizing was conducted using a two-electrode cell with a platinum counter electrode. After anodizing, the specimens were washed in milli-Q water and dried in the ambient atmosphere.

Phases in the anodized specimens were identified by a Rigaku, RINT-2000 X-ray diffractometer using Cu Kα radiation (λ = 0.15418 nm) under an α-2θ mode (α = 1°). Cross-sections of the anodized specimens were observed by a JEOL, JEM-2000FX transmission electron microscope operated at 200 kV. Electron transparent sections were prepared employing a Hitachi FB2100 Focused Ion Beam system. The surfaces of the anodized specimens were observed using a JEOL JSM-6500F field emission scanning electron microscope. Compositions of the alloy and anodic films were investigated by RBS, using 2.0 MeV He^{2+} ions supplied by a tandem-type accelerator at Institute for Materials Research, Tohoku University, with detection of scattered ions at 170°. Data were analyzed using the RUMP program [33].

The electrochemical impedance spectroscopy (EIS) study was performed for the specimens anodized to several potentials in the frequency range from 100 kHz to 0.1 Hz with an AC amplitude of 0.1 V in the EG electrolyte containing 0.1 mol dm^{-3} NH_4F and 0.1 mol dm^{-3} H_2O. The EIS data were analyzed using Zview software.

3. Results and Discussion

3.1. Influence of H_2O concentration on film formation

Fig. 1 shows the potential-time responses of the magnetron-sputtered magnesium films during anodizing at a constant current density of 10 A m^{-2} in the EG electrolytes containing 0.1 mol dm^{-3} NH_4F and several concentrations of H_2O. The anodizing potential increases linearly with time up to 200 V when the H_2O concentration is 28 mol dm^{-3} or less with the rate of the potential rise (0.96–1.0 V s^{-1}) being almost independent of H_2O concentration in this concentration range. At the H_2O concentration of 0.1 mol dm^{-3}, the film growth proceeds close to 100% efficiency, which was estimated from the electric charge passed during anodizing and the amount of Mg^{2+} ions in the anodic film, measured by RBS analysis [31]. It is, therefore, likely that the high growth efficiency is maintained at the H_2O concentrations up to 28 mol dm^{-3}. The rate of the potential rise decreases at the H_2O concentration of 33 mol dm^{-3}, and the rate (0.84 V s^{-1}) deviates further to lower values above 120 V. The initial rate of the potential rise is further reduced by further increasing the H_2O concentration, probably because of the reduced growth efficiency. In addition, the potential rise is terminated by film breakdown at low potentials of 80 and 50 V in the electrolyte containing 44 mol dm^{-3} H_2O and in the aqueous electrolyte respectively. It is obvious from these results that the EG electrolytes with H_2O concentrations of 28 mol dm^{-3} or less are suitable for the uniform film growth to high potentials.

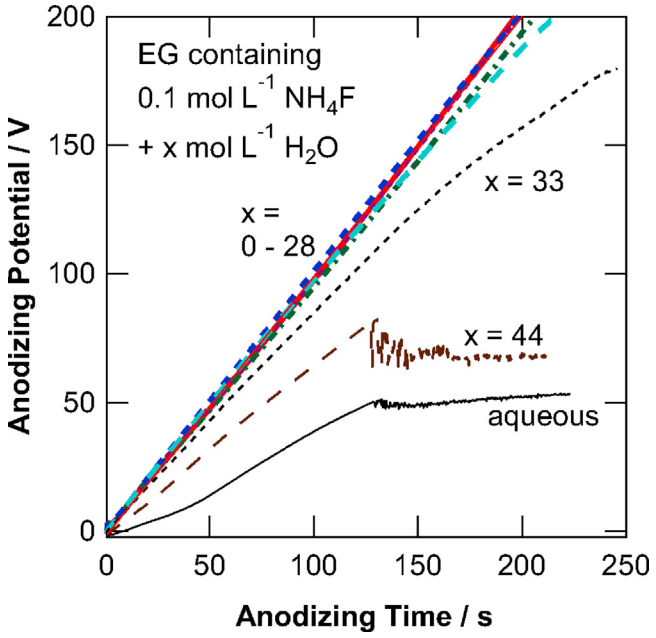

Fig. 1. Anodizing potential-time responses of the magnetron-sputtered magnesium films during anodizing at a constant current density of 10 A m^{-2} in the EG electrolytes containing 0.1 mol dm^{-3} NH_4F and several concentrations of H_2O and 0.1 mol dm^{-3} NH_4F aqueous electrolyte at 293 K.

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