Formation and field-assisted dissolution of anodic films on iron in fluoride-containing organic electrolyte

Khurram Shahzad [a], Etsushi Tsuji [a,b], Yoshitaka Aoki [a,b], Shinji Nagata [c], Hiroki Habazaki [a,b,1,*]

[a] Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
[b] Division of Materials Chemistry & Frontier Chemistry Center, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
[c] Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

A B S T R A C T

Magnetron-sputtered iron films were potentiodynamically anodized at two different sweep rates to 50 V in an ethylene glycol electrolyte containing ammonium fluoride and water. At a high sweep rate of $1.0\,V\,s^{-1}$, a barrier-type anodic film was formed even though the current efficiency was as low as $\sim$50%. In contrast, a nanoporous anodic film developed at a low sweep rate of $0.05\,V\,s^{-1}$, and the film-formation efficiency reduced to 37%. The main part of the anodic films consists of iron (III) hydroxyfluoride with a thin inner layer composed of FeF_3. The inner fluoride layer is formed owing to the faster inward migration of fluoride ions compared to that of the oxygen species. During immersion or re-anodizing of the iron specimen with an approximately 100-nm-thick, barrier-type anodic film at and below 15 V, thinning of the anodic film proceeded uniformly and film dissolution was enhanced by applying an electric field. The impact of the electric field on film formation and dissolution is discussed.

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1. Introduction

Nanoporous oxide films, formed by anodizing valve metals such as Al, Ti, Zr, Nb, Ta, and W, have been extensively explored in the last two decades because of their practical importance as well as of fundamental interest in the growth mechanism. These films have potential applications in corrosion protection, nanodevices, solar cells, batteries, and templates for the fabrication of various nanomaterials [1–4]. There are three types of anodic films: barrier-type, nanoporous-type, and nanotubular-type. Their formation depends upon the anodizing conditions, such as the anodizing electrolyte and anodizing voltage/current. The barrier-type anodic films are typically formed when growth proceeds at a high current efficiency. When the films are amorphous, new film materials are developed both at the film/electrolyte and metal/film interfaces by outward migration of cations and inward migration of anions, respectively, in a corporative manner [5].

The formation behavior of self-organized porous oxide films has attracted much attention in recent years. It is well accepted that porous anodic films are formed when new film material is formed only at the metal/film interface, while cation species migrating outwards are ejected directly to the electrolyte at the film/electrolyte interface [6]. Most recent studies have focused on the understanding of the mechanism of pore generation, and efforts have been made to resolve the causes of field-induced and stress-induced instabilities at the film/electrolyte interface, which lead to pore formation [7–10]. It is generally presumed that pores initiate at a rough film/electrolyte interface under an electric field, where the field is non-uniformly concentrated at the troughs of the film/electrolyte interface. Various mechanisms have been proposed for the growth of porous oxides over the past 50 years, namely (a) field-induced dissolution, (b) field-assisted ejection, and (c) field-assisted plastic flow [6,8,11,12]. In the field assisted dissolution model, first proposed by Hoar and Mott [13], it is presumed that the generation of pores is associated with the dynamic equilibrium between the rate of oxide formation at the metal/film interface and the dissolution of the oxide at the film/electrolyte interface. Most investigations in the field-assisted dissolution model assume that steady-state film growth kinetics occur due to an accelerating dissolution of the oxide film under the influence of a high external electric field at the pore base [6,11,13,14].

Recently, Garcia et al. proposed that the generation and growth of a porous anodic structure on aluminum is associated with the field-assisted flow of oxide material by a distribution of

compressive stresses [12,15–18]. Through a series of tracer experiments, they concluded that pores are generated by plastic flow of material from the pore base towards the cell walls in certain electrolytes. In parallel, Hebert and co-workers support their flow model using a computational approach [8,19].

In both field-assisted dissolution and field-assisted flow models, the electric field applied in the barrier layer sandwiched between the porous layer and metal substrate plays a crucial role. Direct experimental evidences of the influence of the electric field on dissolution and pore initiation and the presence of a critical field for pore initiation during the anodizing of aluminum have been demonstrated recently by Oh and Thompson [9]. They showed that uniform thinning of the oxide film occurs below a field of 7.46 MV cm^{-1}, and field-induced instability and pore initiation start at this critical field. The mechanical instability that leads to major pore formation begins at 8.9 MV cm^{-1}.

As mentioned above, porous anodic films can be formed on a range of metals. Fluoride-containing organic electrolytes with a small amount of water have been often used for the formation of porous anodic films on titanium [20], zirconium [21], niobium [22], and iron [23–27]. The nanoporous and nanotubular anodic films formed on iron have attracted attention due to their future promising applications, including photoanodes for water splitting, electrodes for lithium ion batteries, gas sensors, and electrodes for electrochemical capacitors [27–32]. Photo-electrochemical characterization of as-anodized and thermally treated anodicfilmson iron was also carried out in details [33]. Despite extensive investigations on the mechanism of porous film formation on aluminum, studies on the formation mecha-nism of porous anodic films on iron have been very limited [23–25].

In the present study, we first formed barrier-type and nano-porous-type anodic films on iron by potentiodynamic anodizing in an ethylene glycol electrolyte containing ammonium fluoride and water, and their formation behavior was examined. Then, the influence of an electric field on dissolution rate of anodic films on iron was investigated by applying an electric field to the pre-formed barrier-type anodic film in order to elucidate the crucial role of the electric field in anodizing iron.

2. Experimental

Iron thin films of $\sim$ 460 nm thickness were prepared by DC magnetron sputtering. The target was a 99.9% pure iron disk of 0.5 mm thickness and 100 mm diameter bonded on a copper backing plate. Glass plates and electropolished, anodized aluminum sheets were used as the substrate. The latter substrates were used for Rutherford backscattering spectroscopy (RBS) analysis.

The iron thin films were potentiodynamically anodized at varying sweep rates (1.0 and 0.05 V s^{-1}) in a two-electrode cell with a platinum sheet as the counter electrode. The electrolyte was ethylene glycol (EG) containing 0.1 mol L^{-1} ammonium fluoride and 0.1 mol L^{-1} water at 273 K. After anodizing, the specimens were washed in EG and then in acetone. The relatively low temperature and low water concentration in the electrolyte was selected to reduce the chemical dissolution rate and to promote the formation of a barrier–type film to higher formation voltages.

The surfaces and cross-sections of the anodized iron specimens were observed using a JEOL JSM-6500F field emission scanning electron microscope operated at an accelerating voltage of 10 kV. The composition of the anodic films were determined by RBS using a He^{2+} ion beam of 2.0 MeV energy supplied by a tandem-type accelerator at Tohoku University. The RBS data were analyzed using the RUMP program [34].

3. Results and discussion

3.1. Potentiodynamic growth of anodic films

Magnetron-sputtered iron films were potentiodynamically anodized to 50 V at 1.0 and 0.05 V s^{-1} in the EG electrolyte containing 0.1 mol L^{-1} NH$_4$F and 0.1 mol L^{-1} H$_2$O at 273 K. The typical current-voltage responses are shown in Fig. 1. Initially, the current density increases almost linearly to a current peak, followed by a current decrease to a steady-state current density. At the potential sweep rate of 0.05 V s^{-1}, a second small current peak appears at 12 V, in addition to the first higher current peak at 4 V. Assuming that uniform thickening of the anodic film occurs, the growth of the barrier anodic film can be described by the following equation,

$$\frac{dV}{dt} = E\frac{dh}{dt} \tag{1}$$

where V is the applied voltage, t is the anodizing time, E is the electric field across the anodic film, and h is the thickness of the anodic film. Considering Faraday's law, the following equation can be described,

$$\frac{dV}{dt} = \frac{\eta EMi}{zF} \tag{2}$$

where η is the current efficiency for film growth, M is the molar volume, i is the anodizing current, z is the equivalent number, and F is Faraday's constant. This equation suggests that under a constant potential sweep rate (dV/dt = constant), current becomes constant under a steady state condition, as in the case of Fig. 1. The presence of the current peak at a low voltage region during potentiodynamic anodizing has been found often in the anodizing of valve metals. The phenomenon was well discussed in a review paper by Lorengel [35] and explained in terms of a delayed oxide formation.

Although there are only limited studies on anodic film growth under potentiodynamic conditions [36–38], Curioni et al. poten-tiodynamically anodized high purity aluminum in a sulfuric acid electrolyte [36]. In contrast to the observation of a steady-state current in the present study, they found a continuous current increase above a narrow plateau potential region less than 3 V. This was interpreted by the flow model, which was valid in anodizing aluminum in sulfuric acid [7,39]. Because of the flow of film material, part of the anodic oxide generated at the metal/film interface is displaced to the cell walls. The displacement tends to reduce the thickness of the barrier layer, contributing to an increase in the electric field and current density. Even though a porous film is formed at the low potential sweep rate as indicated
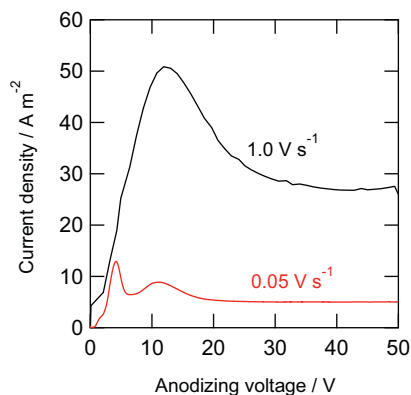

Fig. 1. *I-V* responses of magnetron-sputtered iron films at potential sweep rates of 0.05 and 1.0 V s^{-1} in an EG electrolyte containing 0.1 mol L^{-1} NH$_4$F and 0.1 mol L^{-1} H$_2$O at 273 K.