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Formation Behavior of Nanostructured Anodic Films on Metals in Fluoride Containing Organic Electrolytes

(フッ化物含有有機電解液中における金属上へのナノ構造アノード酸化皮膜の生成挙動に関する研究)

Porous anodic alumina films with self-ordered nanopore channels have been used for surface treatment of aluminum and its alloys to improve corrosion and wear resistance. The films are also of recent interest as key materials for nanodevices and as template for fabrication of nanomaterials. Self-ordering electrochemical anodizing has been recently extended to other metals including titanium, zirconium, niobium, iron and stainless steel, and these nanostructured anodic films have many promising applications. The extensions to many metals and alloys were mainly achieved by finding novel organic electrolytes containing fluoride and small amounts of water. Although extensive studies on formation mechanism of porous anodic alumina films formed in aqueous acid electrolytes have been conducted, little is known about the growth mechanism of the anodic films in the organic electrolytes, particularly on iron that is the most important practical metal. Understanding the growth mechanism is of significant importance to control the morphology and composition of the anodic films. Thus, this study focused on elucidating the growth mechanism of the nanostructured anodic films on iron. Further, in this study it was found that the fluoride-containing organic electrolytes with a wide range of water concentrations are suitable for the formation of compact, so-called barrier-type anodic films on magnesium, which is also a practically important light metal.

This dissertation includes six chapters. Chapter 1 describes the general introduction of anodizing and objective of this dissertation. In chapter 2, the preparation of materials and experimental conditions employed for this study as well as major characterization techniques were described in detail.

Chapter 3 describes the critical factors influencing the film morphology and growth mechanism on the anodic film on iron. Water concentration in electrolyte influences largely the film structure and composition of the anodic film as well as the distribution of fluoride-rich layer within the anodic film. For instance, scalloped metal/film interface, typical of porous anodic alumina, was observed only when the water concentration was $\geq 1.5 \text{ mol dm}^{-3}$. At lower water concentrations the interface became flat. A thinner barrier layer beneath the porous layer was formed by an increase in water concentration. Carbon and fluoride

incorporations were also suppressed at high water concentration. TEM observations clearly disclosed that fluoride enrichment occurred at the cell boundaries as well as at the scalloped metal/film interface when the water concentration was 1.5 ml dm^{-3} . The preferential dissolution of fluoride-rich cell boundaries caused the development of self-ordered nanotubular anodic films at high water concentrations. In contrast, no fluoride enrichment was found at cell boundaries when the water concentration was low (0.1 mol dm^{-3}). Thus, no nanotubular film was formed at low water concentrations. Through the findings in this chapter, a transition of the growth mechanism from “field-assisted dissolution” to “field-assisted flow” with water concentration was proposed.

In Chapter 4, a barrier-type anodic film was formed on magnetron-sputtered iron by employing potentiodynamic anodizing at a relatively fast sweep rate, and the influence of electric field on the dissolution of the barrier-type anodic film was examined. It was found from Rutherford backscattering spectroscopy that the barrier-type anodic film formed in ethylene glycol electrolyte containing $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{F}$ and 0.1 mol dm^{-3} water consists of two layers, comprising an outer iron hydroxy-fluoride layer and an inner iron fluoride layer, with the latter layer forming as a consequence of the faster migration of fluoride ions in comparison with oxygen species. The barrier layer was formed even at a current efficiency as low as 49%. The application of electric field to the barrier-type film on iron accelerated the chemical dissolution of the anodic film at the film/electrolyte interface. Below the critical field of approximately 2.8 MV cm^{-1} , uniform thinning of the anodic film occurred due to field-assisted dissolution, while a nanoporous film was developed above the critical field. The critical field for anodic film on iron is much lower than that recently examined on aluminum ($\sim 5.5 \text{ MV cm}^{-1}$).

In chapter 5, the uniform growth of barrier-type anodic film on magnetron-sputtered magnesium was examined in fluoride and phosphate-containing ethylene glycol- H_2O mixed and aqueous electrolytes. The addition of phosphate to fluoride-containing organic electrolytes induced amorphization of anodic film and increases the volume expansion factor. The anodic films consisted of phosphate-incorporated oxyfluoride and the concentration of incorporated phosphate decreased gradually with an increase in water concentration. The anodic films consist of two layers with an inner layer containing less amount of phosphate. The outer layer is formed at the film/electrolyte interface by the migration of Mg^{2+} ions outwards, while the inner layer is formed at the metal/film interface. The efficiency of film growth reduced from 100 % at $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{O}$ to $\sim 52\%$ in aqueous electrolyte. Despite the low efficiency in aqueous electrolyte, a barrier-type anodic film with a uniform thickness was developed. The reason for the formation of the barrier-type anodic film, not the porous-type film, at such low efficiency was discussed.

Chapter 6 is the general conclusion of this dissertation and future prospects of anodizing research are described.

Considering these research achievements, we conclude that the author is eligible to receive a doctoral degree of engineering from Hokkaido University.