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学位論文題目	Investigation on Growth and Performance of Anodic Aluminum Oxide Film Fabricated in Etidronic Acid under High Current Density （高電流密度下でエチドロン酸により作製された陽極酸化 Al_2O_3 膜の成長と性能の評価）
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論 文 内 容 要 旨

Anodizing aluminum and its alloys in acidic electrolyte solutions results in the formation of anodic aluminum oxide (AAO), or porous anodic alumina (PAA), with numerous nanometer-scale pores. It is generally believed that the structure and performance of AAO films strongly depend on the type of electrolytes (chromic, sulfuric, oxalic and phosphoric acids, etc.), in which the films are fabricated. Most recently, many novel properties obtained via anodizing in newly discovered etidronic acid (HEDP) are attracted more and more attention, such as submicrometer-scale array, structural coloration, high hardness and corrosion resistance. In this work, the anodizing behavior in etidronic acid was systematically investigated by changing current density, electrolyte temperature and anodizing duration. Moreover, in order to broaden the application fields of HEDP anodized film, the hard anodizing was developed on the commercial aluminum alloy.

In chapter 1, the research backgrounds, research significance, summary of the research and the construction of this thesis are described. The objectives of the research are to study the anodizing behavior in etidronic acid and the properties of the resultant film.

In chapter 2, the properties of experimental materials, as well as the experimental methods and the characterizations are presented.

In chapter 3, anodic aluminum oxide films and micro-arc oxide (MAO) coatings are generally prepared from different electrochemical regimes. In this work, we prepared a new hard coating with a MAO/AAO double layer structure in HEDP solution by one-step way for the first time. The influence of current densities on the coating structures, elements distribution, phases composition and hardness was systematically investigated. Results showed that the AAO film would not be burnt down until the current density increased up to 8 A/dm^2. A steady sparking was observed when the current density was higher than 4 A/dm^2, and the visible sparks would automatically quench after a while. The obtained oxide coatings had both the outer volcanic resolidified pool structure and inner honeycomb structure, i.e., a MAO/AAO composite coating. EDS results suggested that the concentration of anion contaminants of MAO layer was lower than that of AAO layer. The estimated growth rate of oxide coating increased from 1 to 36 μm/h with the increase of current densities from 1 to 7 A/dm^2. The hardness of inner AAO layer was about 6–8 GPa, which was in contrast with the highest hardness (26.57 GPa) of the outer MAO layer.

In chapter 4, the growth mechanisms of MAO/AAO coating found in chapter 3 were systematically investigated. In this work, anodizing of aluminum was carried out in HEDP solution at high current density with different duration to track the formation behavior of the coating. SEM images indicated that the burning of initial film is actually caused by local oxide cracking due to the increase of compressive stress. The soft spark would appear when voltage reached 300 V, then change to the micro arcs at 400 V, and finally manufacture the outer MAO layer. Hereafter, the automatic extinguishing of micro arcs gives rise to the formation of inner AAO layer. Moreover, it is evidenced that plasma discharge has few contributions to coating thickening. The barrier layer provides the raw materials for the growth of outer MAO layer. Based on these results, the growth mechanism of MAO/AAO coating processed in HEDP is proposed and discussed.

In chapter 5, we selected a commercial aluminum alloy (6063T5) as the object and developed a high-performance anodized film via HEDP hard anodizing. In this work, the mild HEDP anodizing was first investigated at a temperature range of 15–45ºC, just under the burning current densities. The voltage curves and microstructures of the anodized film prepared in HEDP (Eti-film) indicate that 35ºC is the most appropriate temperature for the fast fabrication of Eti-film, in contrast to the MAO coating and the seriously surface-corroded Eti-film prepared at 15 and 45ºC, respectively. Then, the HEDP hard anodizing without burning was successfully conducted via a gradient-increase-current approach, resulting in a high growth rate (~ 2.1 μm/min), low porosity (< 10%), thick barrier layer (~ 510 nm) and branched nanoholes structure of the hard anodized Eti-film. The Eti-films were systematically investigated by scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, transmission electron microscopy, and a nanoindentation tester. In addition, the wear and corrosion resistance of the Eti-film and the hard sulfuric acid anodized film (Sul-film) were compared. The results indicate that the hardness of the Eti-film can reach ~ 11 GPa (~ 1000 $HV_{0.01}$). The better wear resistance of the Eti-film as compared to the currently widely used Sul-film is attributed to the low porosity and less hydrated alumina content of the Eti-film. Moreover, the corrosion resistance of the Eti-film has been found to be 10 times higher than that of the Sul-film. In general, our results suggest a possibility of replacing the pollution-carrying anodizing methods currently used in the industry with the etidronic acid anodizing.

In chapter 6, general conclusions of this dissertation are made.

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論文審査結果要旨

本論文は、近年提案されたエチドロン酸（HEDP）陽極酸化を対象として、高電流密度下での HEDP 陽極酸化皮膜の成長と性能を調査することにより、陽極酸化の技術理論を拡張し、皮膜の実用化を促進することを目的している。本論文は全 6 章で構成されている。

第 1 章では緒論として、陽極酸化に関する既存の研究から本研究の背景を述べ、本研究の目的を示している。第 2 章では材料および試験方法として、陽極酸化皮膜の作製方法およびそれらの性能の測定方法、構造などの分析方法について説明している。第 3 章では、マイクロアーク酸化/陽極酸化（MAO/AAO）二重層による硬質皮膜の形成に世界初で成功しており、その MAO/AAO 二重層皮膜は、外側にクレータープール構造を有し、内側にハニカム構造を有することを明らかにした。AAO 層の硬度は約 6～8GPa であり、MAO 層の硬度が 22GPa 以上を示している。第 4 章では、高電流密度による皮膜焼けと MAO/AAO 二重層皮膜の成長機構を調査している。HEDP 陽極酸化中の皮膜焼けは、皮膜の膨張によって引き起こされることを明らかにし、マイクロアーク酸化と陽極酸化を交互に行うと、MAO/AAO 二重層皮膜が得られることを示した。マイクロアークは、皮膜の成長速度に影響せず、MAO/AAO 二重層皮膜の成長はイオンの移動に由来することを示唆した。第 5 章では、6063T5Al 合金の HEDP 硬質陽極酸化を初めて実現しており、最大 11GPa の硬度を持つ陽極酸化皮膜を超高速で作製している。HEDP 硬質陽極酸化皮膜は、一般的に使用されている硫酸硬質陽極酸化皮膜よりもはるかに優れる耐摩耗性と耐食性を示した。第 6 章は結論であり、研究結果をまとめている。

本論文は学術的および工学的価値が高く、その研究成果は、HEDP 陽極酸化の技術理論を拡張していることから学術的貢献が大きく、HEDP 陽極酸化が高性能皮膜を作製する可能性が示している点で実用面での幅広い波及効果が予想される。また、研究業績として、査読付国際学術論文 3 編、国際会議 1 件、国内会議 1 件を公表している。

よって、本論文は博士（工学）の学位論文として合格と認める。