Effect of Magnetic Field on Anodized Oxide Film without Dielectric Breakdown

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Abstract

Titanium and its alloys have superior properties with the aid of oxide film on the surface. Anodic oxidation is one of the processes that can improve the metal surface. TiO_2 produced by anodic oxidation is expected for applications as biomaterials or functional photocatalysts. In this paper the effect of magnetic field on anodic oxidation of Ti without dielectric breakdown will be investigated for the electrolytes of sulphuric acid aqueous solution and ethylene glycol. The result shows that magnetic field can control the pore diameter and the thickness of the oxide film.

Introduction

Titanium alloys have unique and superior properties such as wear resistance, biocompatibility and corrosion resistance, because of strong and chemically stable oxide film on the surface. Therefore, titanium dioxide has wide of the applications for medical implant [1,2]. On the other hand, nanostructure of TiO_2 film, i.e. pore structure or film morphology, gives useful functions to the oxide film such as a nano-platform, a sensor, a photo-catalyst, etc. [3,4]. Anodic oxidation is one of producing method of TiO_2 film. Many studies have been conducted about anodizing process of titanium, because the surface morphology of TiO_2 film can be easily controlled with low cost.

In electric deposition process, magnetic field can affect the surface morphology of deposited film [5]. It was known that two effects were appeared on the electrochemical reaction induced by magnetic field imposition. The first is MHD effect. The Lorentz force by interaction of electrolytic current and magnetic field causes MHD convection. MHD effect is promotion of mass transfer by this convection. The second is micro MHD effect. Micro MHD effect is caused by micro MHD convection that is occurred near precipitation interface. Micro MHD effect suppresses the individual of crystal nucleation.

In anodizing phenomena, same effect of magnetic field will be expected, especially micro MHD effect can change the size and the shape of the pore in oxide film.

In this paper, the effect of magnetic field imposition on the morphology of anodized oxide films investigated using superconducting magnet. Basic phenomena of metal oxidation and pore formation in the anodized film on Ti plate will be revealed from the experiments of metal anodization from sulfuric acid and ethylene glycol with ammonium fluoride.

1. Experiments

Fig. 1 shows the flow of the experiment procedure. Pure titanium plate was exposed chemical polishing firstly and then ultrasonic cleaning in acetone. Using this Ti plate, metal anodization experiments were conducted. The surface morphology and the pore structure were observed by use of FE-SEM. And the crystallographic structure of the oxide film was...
determined by XRD with CuKα radiation. Fig. 2 shows schematic of an anodization cell. The prepared Ti plate was used as an anode and a pure platinum was used as a cathode. Two types of electrolyte was adopted, one is 0.5 M sulfuric acid with 0.1 M ammonium fluoride and the other was 0.3 mass% ammonium fluoride in ethylene glycol. Anodization time was 2h under potential range of 20-40 V for sulfuric acid, and 40-70V for ethylene glycol.

Fig. 1. Experimental procedure                          Fig. 2. Schematic of anodizing cell

2. Results and Discussion

2.1. Sulphuric Acid Electrolyte

In general, anodized oxide film is formed in the inside the original metal surface with the formation of nano-pores in the case of under the critical voltage of dielectric breakdown. Fig. 3 shows the schematic drawing of the mechanism of oxide film formation with pores in porous layer and barrier layer.

Actual anodizing behaviour is composed of metal oxidation and dissolution of oxide layer. At the inner surface of pores, especially at bottom surface, TiO₂ can be dissolved by fluorine ion in following reaction due to anodization voltage.

\[
\text{TiO}_2 + 6\text{F}^- = \text{TiF}_6^{2-} + 2\text{O}^2- \quad (2.1)
\]

Oxygen ion generated by the reaction (2.1) diffuses from the pore bottom to the interface between oxide film and metal Ti through barrier layer and oxidizes Ti as anodic oxidation of following reaction.

\[
\text{Ti} + 2\text{O}^{2-} = \text{TiO}_2 + 4\text{e}^- \quad (2.2)
\]
Fig. 4 shows typical anodized surfaces for anodizing voltage of 20V and 30V, in the case without magnetic field and with magnetic field of 5T. In these photos, small pores of about 20nm diameter can be observed. These pores appear in every condition of anodization in almost same size, but in the case of no magnetic field, the surface morphology is rougher than that with magnetic field.

(a) 20V, no magnetic field
(b) 20V, magnetic field:5T
(c) 30V, no magnetic field
(d) 30V, magnetic field:5T

Fig. 4. FE-SEM images of anodized surface for various anodizing voltage

Fig. 5 shows XRD patterns of anodized Ti plate. In Fig. 5 (b), there is no peak of anatase titanium dioxide in 20 V because anodic oxide layer is thin. In 30 and 40 V, there are broad peak of anatase TiO\textsubscript{2} in both no magnetic field and magnetic field of 5T. The oxide layer thickness increased as increase of the applied voltage.

(a) no magnetic field
(b) magnetic field:5T

Fig. 5. XRD patterns of Ti under anodization voltage of 20, 30, and 40V
Tab. 1 shows crystallite size of anatase TiO$_2$ (101) of specimens. Crystallite size of anatase TiO$_2$ (101) in magnetic field is smaller than that in no magnetic field. In previous study, grain refinement by micro MHD effect was reported [5]. Also in this study, it is believed that the crystallite size is smaller by this effect.

Tab. 1. Crystallite size of anatase TiO$_2$(101).
(a) without magnetic field and (b) with magnetic field (5T)

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.27</td>
</tr>
<tr>
<td>30</td>
<td>8.84</td>
</tr>
<tr>
<td>40</td>
<td>8.91</td>
</tr>
</tbody>
</table>

2.1. Ethylene Glycol Electrolyte

Anodization process under ethylene glycol solution is more stable so that the critical anodization voltage for dielectric breakdown increases up to over 70V. It is found that this electrolyte is advantageous for rapid formation of a uniform oxide film. Fig. 6 shows the typical anodized surfaces for anodizing voltage of 50V and 70V, in the case without magnetic field and with magnetic field of 5T. In these photos, regularly aligned pores can be seen and the size becomes large as increase of anodization voltage because of the promotion of the reaction (2.1). Furthermore, imposition of magnetic field can increase pore size. Micro MHD effect also appears here, so as to promote the reaction (2.1).

![Fig. 6. FE-SEM images of anodized surface in ethylene glycol electrolyte](image)

Micro MHD effect can promote a chemical reaction relating electron exchange. In the configuration of these experiments, magnetic field is imposed to be perpendicular to the metal surface, so MHD effect can not be expected. However, microscopic eddy motion appears in each pores depending on the bottom shape of pores. At the bottom, the shape is not flat as...
shown in Fig. 3. Electric current of anodization almost vertical direction but some part of the current leaks into the wall and horizontal component appears especially in bottom part. The interaction of this horizontal component of an electric current with a strong magnetic field yields rotating Lorentz force in nano-pores. This microscopic eddy flow can promote the transfer of ions so that the anodization reaction can be promoted. Fig. 7 shows the cross sectional views of oxide films. As indicated in the figure, nano-pores form straightly and the film thickness increase as increase if anodization voltage.

Fig. 7. FE-SEM images of cross sectional view of oxide film

Fig. 8 shows the oxide film thickness increases with increase of anodization voltage. The effect of magnetic field imposition appears in relatively high voltages as shown in Fig. 8.

Fig. 8. Effect of magnetic field imposition on oxide film thickness

The size of nano-pores is so small that the flow in the pore suppressed by viscosity. Because the suppression effect becomes strong in long pore in thicker film, the growth rate decreases
for thicker oxide film. On the other hand, in the case of magnetic field imposition, microscopic eddy flow can help the transfer ions from the bottom to the outer of the film.

**Conclusions**

Metal anodization process under strong magnetic field is proposed. Basic experiments were conducted for titanium in sulphuric acid aqueous solution and ethylene glycol solution as an electrolyte. Obtained results can be summarized as follows:

1. Regularly aligned pores appear on the oxide film with the aid of fluorine ion and the surface morphology in aqueous solution is rougher than that in ethylene glycol solution, because the anodization phenomena is stable in that solution.
2. Micro MHD effect can promote the anodization reaction, for aqueous solution, the crystallite size becomes small by the imposition of magnetic field. For ethylene glycol solution, pore size becomes large due to micro MHD effect.
3. In the case of ethylene glycol electrolyte, magnetic field can promote the transfer ions due to microscopic eddy flow.

**References**


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