The Effect of Magnetic Field on Metal Anodizing Behaviour

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Abstract
Metal anodizing process has been utilized in various surface treatments. In the field of biomaterials, in order to improve biocompatibility with biological tissue, metal anodizing of titanium or zirconium has been adopted. In the former work with imposition of intense electric field, it is found that the electric field increases the anodizing reaction rate, and the suitable range of anodizing voltage for obtaining preferable surface morphology becomes wider. On the other hand, magnetic field can promote the metal substitution reaction and it also increase the metal anodizing. Furthermore, magnetic field has the possibility of ordering the pore arrangement in the anodized film. Metal anodizing experiments using phosphoric acid solution is conducted under parallel and vertical magnetic field imposition up to 1T. It is found that magnetic field can promote the anodizing reaction and pore formation. On the other hand, vertical magnetic field can promote the anodizing reaction heterogeneously in relatively low voltage. For high voltage of 300V, the pore morphology ware almost same for the cases of without magnetic field, parallel magnetic field imposition and vertical magnetic field imposition, but the shape and the size becomes uniform in the case of magnetic field imposition. Magnetic field is effective not only the promotion of the anodizing reaction but also the homogenization of pore formation due to MHD and micro MHD effect.

Key words : metal anodization, magnetic field imposition, bio-materials

Introduction

In the field of biomaterials, titanium or zirconium alloys are mainly used because of their good biocompatibility and Young's modulus close to the bone tissue. In order to increase the performance of biomaterials, metal anodizing has been conventionally adopted as a surface treatment, where the anodized oxide film can be divided into two morphologys. One is microscopic honeycomb structure under lelatively low anodizing voltage, and the other is porous structure due to dielectric breakdown phenomena under high anodizing voltage. From a biocompatibility standpoint, porous anodized film more preferable, and the size and regularity of pore arrangement are strongly releted with the biocompatibility. Many researchs has been done with various anodized voltage and the electrolytes[1].

In this study, the effect of magnetic field imposition on the morphology of anodized oxide film is investigated using superconducting magnet. In former work, it is found that an electric field imposition has some influence on the critical anodizing voltage for dielectric breakdown and the regularity of pore arrangement in the anodizied film[2]. On the other hand, in the condition of magnetic field imposition, MHD effect or micro MHD effect can be expected as the same way in electro-deposition behavior of cathode electrode[3][4]. In this paper, 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 pphosphoric acid with the anodized voltage up to 300V. Furthermore in order to clarufy the effct of magnetic field imposition, Ti anodizing experiments will be conducted where the anodizing cell will set in the bore of superconducting magnet. The properties of anodized film will be investigated using XRD and SEM.

Experiments

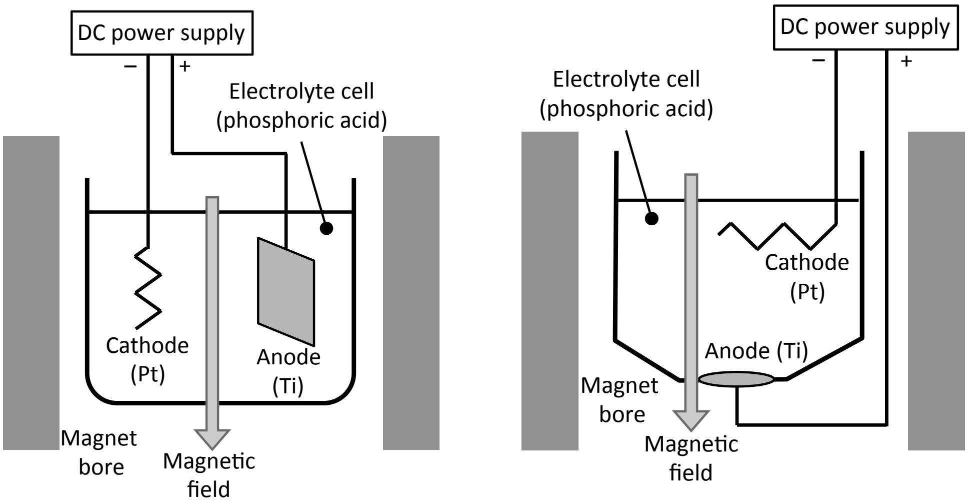
In the preparation of anode plate, a titanium plate is polished with silicon carbide and diamond paste and cleaned with an ultrasonic device. Metal anodizing of Ti plate is conducted in potentiostatic mode with the electrolyte of 1.0 mol/L phosphoric acid and various anodizing voltage up to 300V. Fig.1 shows the schematic drawing of an experimental cell in the magnet bore in the case of (a) parallel magnetic field and (b) vertical magnetic field. The strength of magnetic field is up to 1T. The reactions on the both electrode surfaces are considered to be ;

$$\text{Cathode : } 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1}$$

$$\begin{aligned}\text{Anode : } 4OH^- &\rightarrow H_2O + O_2 + 4e^- \\ Ti + O_2 &\rightarrow TiO_2\end{aligned} \tag{2}$$

Actual anodic reaction is very complicated including ionization and discharge. And in the range of over the critical voltage for dielectric breakdown where many pores appears in the oxide film with micro arc causing to heat generation.

Anodized oxide film around the pore melted by the heat and it is precipitated again around the pore resulting smooth pores. That is considered to be advantageous for the biocompatibility. In order to ascertain the pore formation and pore arrangement, surface oberbation is conducted using SEM. Furthermore, thin film XRD measurements is conducted to examine the oxide formation on the anode plate.

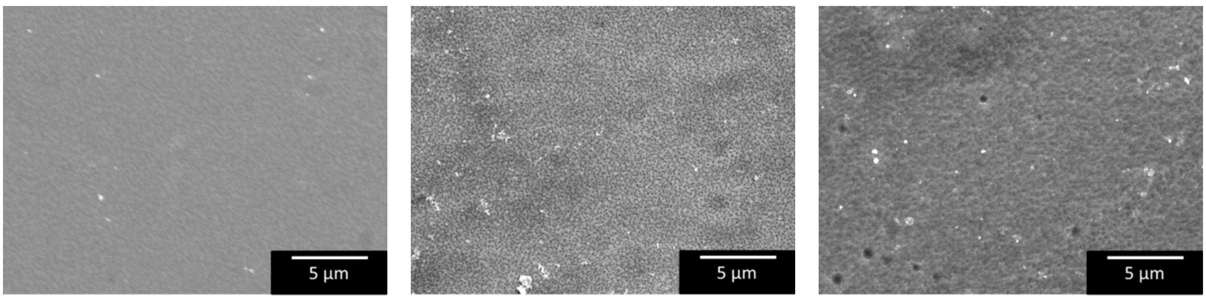


(a) Parallel magnetic field (b) Vertical magnetic field

Fig.1 : Schematic of metal anodizing cell in the magnet bore.

Results and Discussion

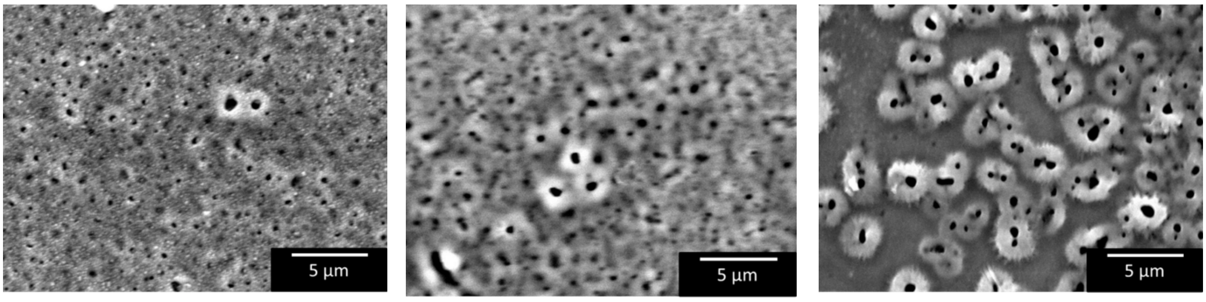
In the range of under the critical voltage for dielectric breakdown, the surface morphology becomes bumpy by imposing magnetic field with many submicron pores. And the uniformity of the pore size and arrangement is better in the case of parallel magnetic field than that in vertical magnetic field as shown in Fig,2. In the parallel magnetic field, anodizing electric current is perpendicular to magnetic field, so that the strong convection appears in the vicinity of anode surface. This MHD effect can promote the oxidation reaction due to the increase of mass transfer. In the vertical magnetic field, MHD effect can not be expected, but micro MHD effect can promote the oxidation reaction which is not so strong under 1T magnetic field.



(a) without magnetic field (b) parallel magnetic field (c) vertical magnetic field

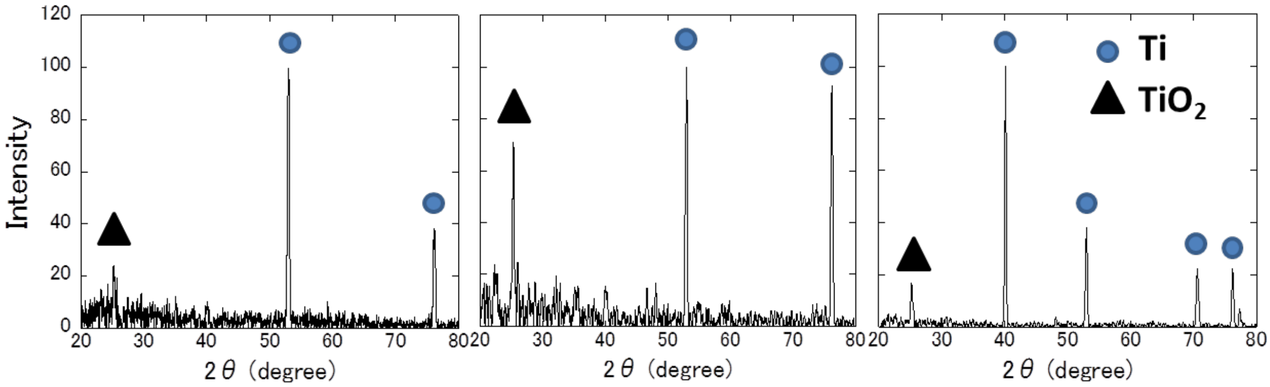
Fig.2 : SEM images of the anodized surface with the anodized voltage of 100V.

In the relatively high anodizing voltage of 150V-250V, dielectric breakdown occurs in the same way regardless of the imposition of magnetic field, but magnetic field affects the pore size and pore arrangement. Fig.3 shows the surface morphology of 200V anodizing voltage without magnetic field and with parallel or vertical magnetic field. The black spots indicate the pores caused by dielectric breakdown, and the pore size increase by imposing magnetic field. In the parallel magnetic field, it seems that the surface is completely covered by oxide in the same way without magnetic field, but the oxide layer becomes thicker. In the vertical magnetic field, pore formation occurs heterogeneously and each pore becomes larger than that with parallel magnetic field. Fig.4 shows the XRD pattern of anodized film.



(a) no magnetic field (b) parallel magnetic field (c) vertical magnetic field

Fig.3 : SEM images of the anodized surface with the anodized voltage of 200V.

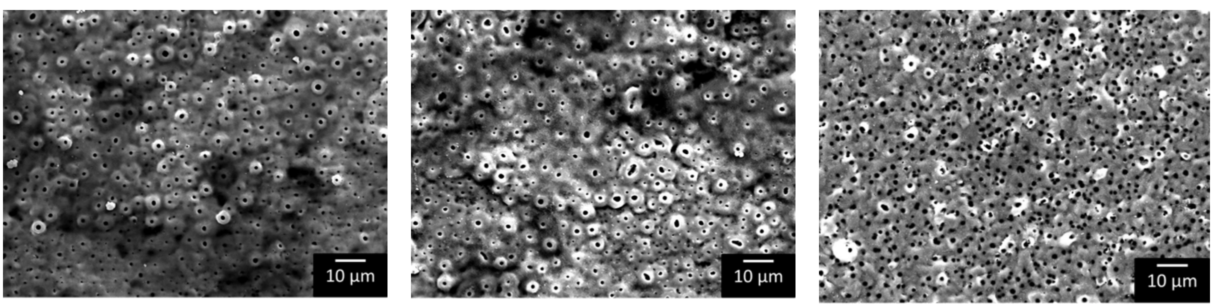


(a) without magnetic field (b) parallel magnetic field (c) vertical magnetic field

Fig.4 : Thin film XRD pattern of the anodized surface with the anodized voltage of 200V.

Because the anodized film is very thin, metallic Ti peaks appears in all patterns. In the case of parallel magnetic field, the peak of TiO_2 is highest, so that the oxidation reaction strongly promoted by MHD effect as shown in Fig.3 (b). In the case of vertical magnetic field, many peaks of Ti indicate the non-uniformity of pore formation as shown Fig.2 (c). In this situation it seems that another mechanism control the pore formation. The electrical conductivity of oxide film is very small, the pore formation should result the non-uniformity of electric current in the vicinity of the anodizing surface. Under the imposition of magnetic field of 1T, the Lorentz force due to the interaction of imposed magnetic field with the transverse electric current. This Lorentz force causes to small vortex flow corresponding with each pore. Mass transfer can be promoted by this vortex flow for a relative large pore. On the other hand, small pore formation is suppressed by this vortex flow. That is the reason of the non-uniformity of large pore as shown in Fig.4 (c).

In relatively high voltage of 300V, pore size and pore arrangement is almost same regardless of magnetic field imposition as shown in Fig.5. However, the anodized surface becomes smooth and the regularity of pore arrangement increase in the case of vertical magnetic field as shown Fig.5 (c).



(a) without magnetic field (b) parallel magnetic field (c) vertical magnetic field

Fig.5 : SEM images of the anodized surface with the anodized voltage of 300V.

Conclusion

In order to understand the metal oxidation and pore formation phenomena in a metal anodizing process aiming to improve the biocompatibility of titanium or zirconium alloys, some Ti plate anodizing experiments using phosphoric acid electrolyte is conducted. And then, effect of magnetic field imposition on the anodizing behavior is examined. The obtained results can be summarized as follows.

- In the range of anodizing voltage before dielectric breakdown, i.e. under the critical breakdown voltage for Ti plate, imposed magnetic field can promote the anodizing reaction and make the surface microscopic bumpy morphology.
- In the range of anodizing voltage over 150V, dielectric breakdown occurs in the same way regardless of magnetic field imposition. And parallel magnetic field can promote the surface oxidation reaction and pore formation uniformly because of MHD effect, but under a vertical magnetic field, pore formation and oxidation reaction becomes heterogeneous.
- In relatively high voltage, pore size and distribution is almost same regardless of magnetic field imposition. However, the anodized surface becomes smooth and the regularity of pore arrangement increase in the case of vertical magnetic field.

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