

Microstructure of Titania Layers Formed by Plasma Electrolytic Oxidation (PEO) Method

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Titania coatings were prepared on commercially pure Ti by plasma electrolytic oxidation (PEO) method with various electrolytes and process condition. Coatings were formed under galvanostatic condition with several current density values, and the change of applied voltage with process time was recorded. The microstructure of the titania coatings was observed using XRD, SEM, TEM, and the time-voltage diagrams were analyzed in terms of microstructure evolution

Keywords : plasma electrolytic oxidation (PEO), titania, TEM, time-voltage behavior

1. Introduction

Plasma electrolytic oxidation (PEO) method can produce thick ceramic coating layers on Al, Ti, Mg, Ta, or Zr, the so called 'valve metals', using the plasma made by micro arc discharge over the break-down voltage.¹⁻⁶⁾ These ceramic coatings can be used to various application, including heat, corrosion, and wear-resistant layers of the metallic substrate. Also, titania coatings on Ti can enhance the biocompatibility of the Ti implants.⁵⁾

Most of researches have been concentrated on Al and its alloys, and produced excellent results, because Al is one of the most important light metals in industry and, fortunately, it has very excellent native oxide, alumina, having excellent physical and chemical properties. Recently, the number of researches focused on Mg and Ti and their alloys are increasing.^{3,7-10)} Mg and its alloys would become more and more important considering the low (virtually the lowest, among the commercial alloys) density and high specific strength. So, studies on the PEO coatings on Mg and its alloys would lead the PEO researches. Researches on Ti can be divided into two main categories, the surface enhancement for biomedical usage (mainly interested in commercially pure Ti like grade 1)^{5,11)} and wear resistance coatings for structural materials (mainly on the surface of Ti-6Al-4V alloy).¹⁰⁾ For biomedical usage, titania coatings having porous surface structure have been studied extensively.^{5,7,11)} To enhance

the bioactivity, various bioceramic materials are composed and incorporated in the coating layer constructing a composite.⁷⁾ In structural Ti alloys, the main purpose of the PEO coating is to endow wear resistance to the Ti alloy substrates, by fabricating composite structure of titania and hard phases like alumina or Al₂TiO₅.¹⁰⁾

In the PEO process, electrochemical and plasma process are incorporated together, and as a result, it is very difficult to analyze or study the mechanism of the process in part or as a whole. However, to control the final quality and performance of the coatings, mainly depending on the surface and microstructure, extensive and intensive researches should be carried out focusing on the mechanism of PEO or basic nature of microstructure evolution. Nevertheless most of PEO researches are focusing on the development of the manufacturing process and investigations dealing with basic nature of the PEO in the microstructural basis are rare compared with the number of application researches.

In this investigation, a basic approach to PEO process of commercially pure grade Ti was tried, adopting time-potential behavior analysis¹²⁾ under galvanostatic mode. In the galvanostatic mode, voltage changes to maintain the steady current, and changes of electrochemical or plasma process and microstructure during the PEO process cause the change of voltage. For the microstructural analysis on the coating structure, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used.

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Table 1. Process conditions of titania formation using PEO.

Sample ID	Electrolyte	Current density J (mA/cm ²)	Max. voltage (V)
AA1	0.4M acetic acid	83	100
AA2	"	"	200
AA3	"	"	350
SC1	0.5M Na ₂ CO ₃	4.3	110
SC2	"	6.0	144
SC3	"	8.5	148
PA1	0.1M H ₃ PO ₄	20	200
PA1P	"	40 (rect. pulse, 50% duty)	100

2. Experimental

Commercially pure Ti of grade 1 was used in this investigation as the substrate for titania coating by PEO method. Ti plate was cut to 10 × 10 × 1 dimension, polished to #2400 emery paper, and rinsed by acetone, ethyl alcohol, and distilled water using ultrasonic cleaner.

0.4 M acetic acid, 0.5 M Na₂CO₃, and 0.1 M H₃PO₄ solutions were used as electrolytes. The specimens were oxidized under galvanostatic mode (constant current DC mode), with several current density values, to analyze the current density effect on the time-potential behavior. The detailed process conditions were listed in table 1.

For the microstructural analysis, the surface of the oxidized Ti was observed using SEM (S-2400, Hitachi and JSM 5600, JEOL). Also, the oxidized samples with various treatment conditions were analyzed by XRD (D8, Bruker). For the TEM observation, samples were prepared by focused ion beam (FIB) system (Nova 600, FEI), and observed with 200 kV (TECNAI G2, FEI).

3. Results

Since the nature of PEO process is very complex, to analyze the process in scientific basis, the system should be simplified and, then, investigated systematically. Under galvanostatic condition, changes of electrochemical or plasma process and microstructure during the PEO process cause the change of voltage, and the time-voltage behavior reflects much about the kinetic nature of the oxidation of a given system. Under constant current condition (galvanostatic condition), as the oxide layer grows, the electrical resistance of the specimen system increases and the potential needed to maintain the set current value increases with time. The time-voltage behavior in the 0.4 M acetic

acid and the surface morphology of the samples were given in Fig. 1. In the figure, the time-voltage curve can be divided into three linear stages and the transition regions between them (fig. 1 (a)). Snizhko et al.¹²⁾ reported that the time-potential behavior of Al can be divided into 4 linear stages and each stage showed different feature during the constant current mode (or galvanostatic) oxidation: the first step, with the maximum slope, corresponded to conventional anodizing process, and in the second stage, gas evolution became vigorous and the slope decreased. In the third stage, the slope of the time-voltage curve increased again and recrystallization of oxide film and defect formation on the surface occurred. With the beginning of the fourth stage, visible arc began to appear and the slope of the curve decreased and showed vigorous serration. In Fig. 1, the time-potential curve can be divided into 3 linear stages, with two transition regions between the three linear stages. Visible arcs and the fourth stage didn't appear to the voltage of 350 V. In Fig. 1 (b)~(d), with the increment of maximum voltage, the surface of the specimens became more rough and showed coarser defects on them. It is obvious from fig. 1 that the time-voltage behavior of the PEO process under constant current mode had close relationship with the electrochemical reaction and the change of the coating layer.

In Fig. 2, PEO results using 0.5 M Na₂CO₃ solution for the electrolyte were drawn. In Fig. 2 (a), the effect of the current density was shown. As the current density increased, the slope of the second and third stages of the time-voltage curve increased and when the current density was 8.5 mA/cm², the duration time of the second stage decreased so that the distinction of the second stage became meaningless in practical manner and the time-voltage behavior can be divided into two stages of different slope. However, the voltages corresponding to the onset of each stage didn't show any remarkable dependency upon current density.

During PEO process, different kinds of oxides are formed and transit to other phases with process variables. In this investigation, oxide phase formation and transition behavior under galvanostatic mode are the primary concern. The microstructural evolution during galvanostatic mode PEO process was shown in Fig. 2 (b) and (c). As shown in Fig. 2 (b), specimens treated to 50 and 75 V were in the stage 3, to 110 V in the transition region between stage 3 and 4, and specimens treated for 12 and 20 min are in the stage 4. In Fig. 2 (c), at the final voltage of 75 V, a broad peak, which was not characterized, appeared and with the increment of final voltage and treatment time, anatase started to be composed, and when treated to stage 4, at which oxidation occurs with visible

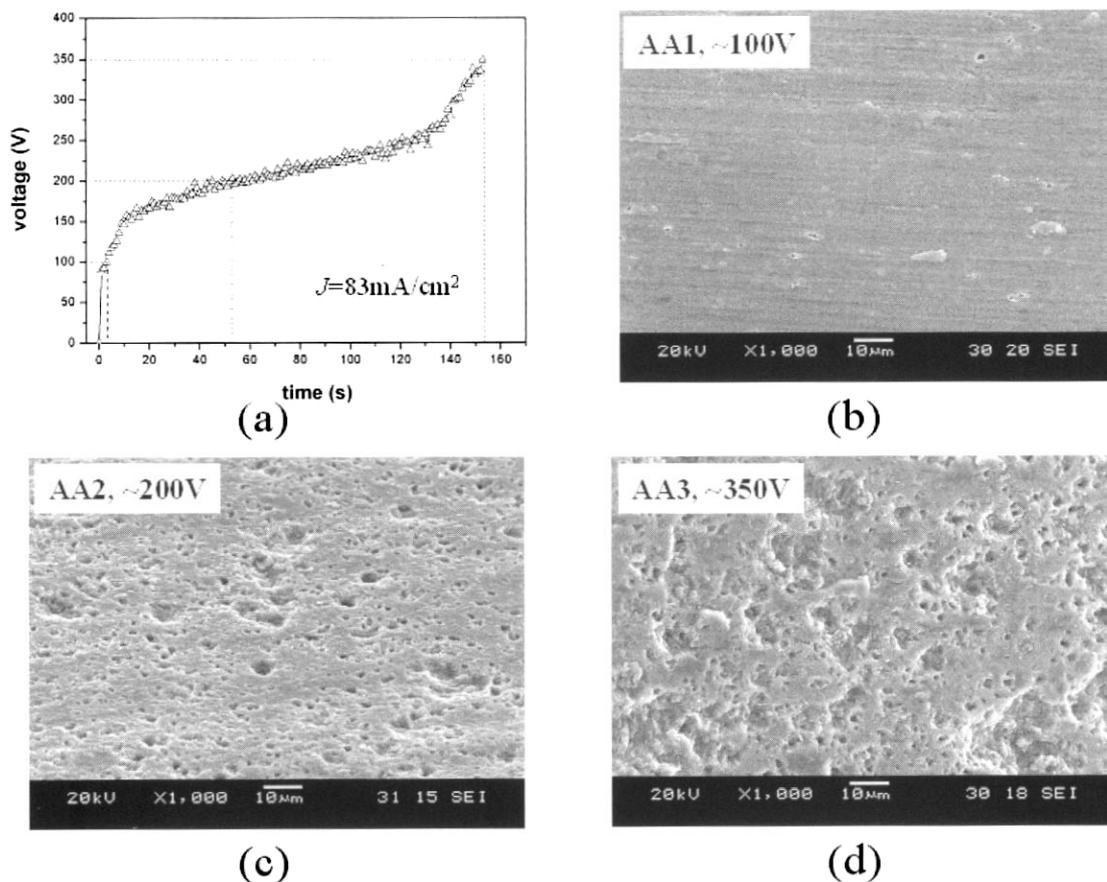


Fig. 1. Time-voltage behavior using 0.4M acetic acid and surface morphology of titania with various maximum voltages.

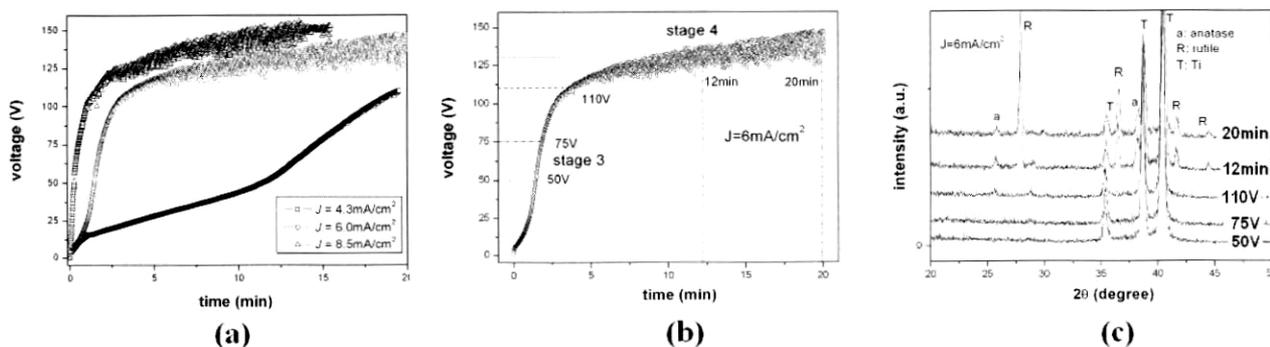


Fig. 2. (a) Time-voltage behaviors using 0.5M Na_2CO_3 with various current density values. (b) Time-voltage curve for current density of $6.0\text{mA}/\text{cm}^2$. (c) XRD results with several maximum forming voltages for current density of $6.0\text{mA}/\text{cm}^2$.

arc on the specimen surface, the fraction of rutile phase increased drastically. The sequence of the titania formation is thought to be as following: amorphous \rightarrow anatase \rightarrow rutile.

In our galvanostatic PEO experiment, the onset of the arc was difficult to determine, because, at the onset of arcs, they were so tiny as not to be visible easily with

naked eyes. Also, when we analyzed the time-voltage behavior, during the transition from one stage to the next one, the change of the potential was not sharp and relatively large portion of the curve lies outside of the linear region. So, more attention to the kinetic research in the transition region should be paid.

4. Discussions

Although the time-voltage behavior of the PEO process of Ti under galvanostatic mode showed four stages of different slopes, the onset of the arc plasma was not clear in the curve. Also, XRD could show the evolution of oxide phases, it couldn't be applied to the early stages of oxide formation, in which the thickness of the titania was not thick and the crystallinity of the oxide phases were poor to form sharp and distinct peaks. Transmission electron microscopy (TEM) can be a powerful tool for the analysis of the initial crystallization stages, especially stage 2 or 3 in the time-voltage curve. In this investigation, PEO titania film formed in the 0.1 M H₃PO₄ solution was observed by TEM. In Fig. 3, time-voltage curves of Ti sample in the 0.1 M H₃PO₄ solution were drawn. Two types of current modes were used: a constant or steady current just like in Fig. 1 and 2, and rectangular pulse of fixed current with a frequency of 100 Hz and duty cycle of 50%. With the on/off behavior of the current, voltage changed to satisfy the condition of current, and the average voltage of each data acquisition interval, 1s, was recorded. The time-voltage behavior of the current pulse had some common nature with that of the steady current: the initial inflection around 20 V, 30 V, and 150~170 V region. However, voltage behavior of the pulse current showed another inflection point around 90 V. More careful PEO experiment in the darkroom, a continuous medium of fluorescence-like light emission could be observed at the specimen surface at that voltage, and brighter visible arcs were detected around 150 V, which was close to the inflection point of the voltage curve for the steady current, about 170 V and the beginning of the fourth stage. In Fig. 4, TEM images of the PEO film, with maximum treatment voltage marked in Fig. 3, were shown. In the left figure of Fig. 4, the whole cross-section of the oxide film was drawn from the Ti substrate, passing some bubbles (around B) and some crystalline phases (region C), and a macro pore (A), and amorphous top layer and finally to the Pt layer, deposited to protect the oxide sample surface during the sampling process in the FIB system. Some bubbles were observed near the Ti/titania interface,¹³⁾ and from the high resolution image (upper right) it was found that the oxide around the bubbles were amorphous titania. Bubbles were also found in the middle region and around the bubbles were some nanocrystalline titania grains (C in the left figure). From the selected area electron diffraction (SAD) result in Fig. 4, it can be found that the nanocrystals were mixtures of anatase and rutile. Also, while the spots from anatase {101} are bright and clearly detected, those from the rutile {110} are dim and unclear. So, it is thought

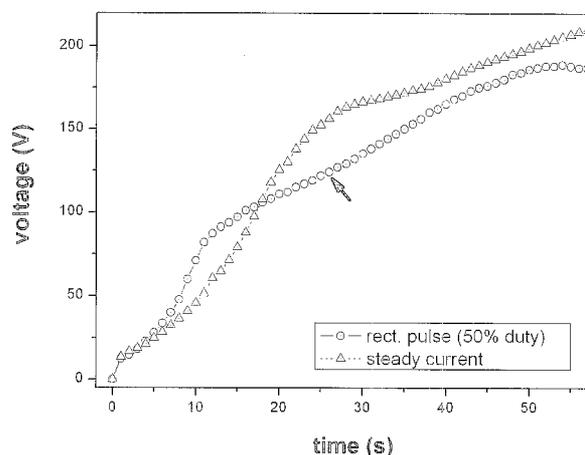


Fig. 3. Time-voltage behaviors using 0.1M H₃PO₄ under steady current and rectangular pulse current.

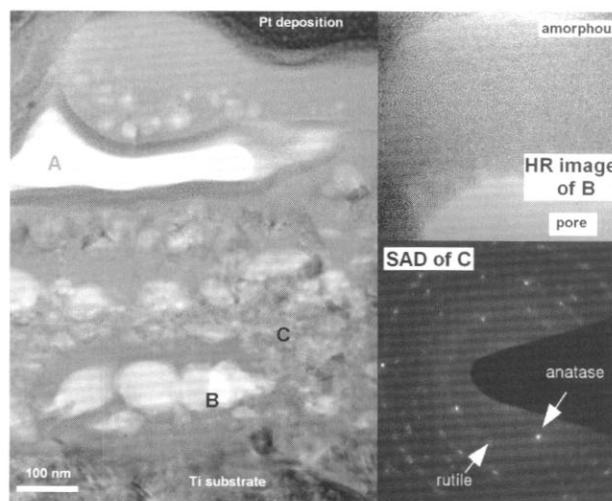


Fig. 4. TEM image of the cross-section of the titania coating formed by PEO method and the high resolution image and the SAD pattern of B and C point in the left figure respectively.

that anatase crystals are formed first and rutile phase appears later. However, we didn't get any clear information for the same titania sample by XRD. So, it can be inferred from Fig. 3, 4 and the observation in the darkroom that the recrystallization process in the third stage is related to the onset of fluorescence-like medium of micro arc, not easily detectable in ordinary experimental condition, and the onset of the fourth stage is due to the appearance of the macro and visible arc. So, more careful observations of the voltage behavior as well as extensive microstructural analysis are needed to reveal the mechanism of the oxide formation and their evolution in PEO process.

5. Conclusions

The time dependency of the voltage during the galvanostatic PEO was investigated. The time-voltage behavior showed four linear stages and the transition regions among them. The boundaries among the linear stages in the time-voltage curve were not clear. With XRD results, the crystallization behavior of the oxide could be characterized, mainly from the third and fourth stages and it was observed that the amorphous phase was formed first, and then, the nanocrystalline anatase and rutile phases appeared with the increment of final treatment voltage and time. TEM analysis on the transition region between stage 3 and 4 was carried out, and the microstructure of the whole oxide cross-section was observed and characterized. From the elaborate observation of the specimen surface and the time-voltage curve along with the microstructural analysis, it can be concluded that the recrystallization in the stage 3 is related to the micro arc media on the specimen surface, not easily observable in usual condition and appearing before the macro visible arc.

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