Formation of Nano-Structured Oxide Layers Formed on Ti-Fe Alloys by Anodization

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The present work reports the anodization of Ti-Fe alloys in a fluoride-containing ethylene glycol electrolyte and the morphology of resulting anodic oxide layers. The current density generated during the anodization at voltages ranged from 10 V to 50 V significantly decreases in the early stage, then increases once and finally exhibits gradual decrease with time although the magnitude of the current depends on the alloy composition. On pure Ti and Ti-10 at% Fe alloy, anodic oxide layers show a nanotubular structure at all applied voltages. On the other hand, at lower voltages, nanotubular oxide layers are also formed on Ti-50 at% Fe and Ti-70 at% Fe alloys, but at higher voltages the morphology of anodic oxide layers changes to an irregular-shaped porous structure. These results indicate that the morphology of anodic oxide layers is affected not only by the alloy composition but also by applied voltage.

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1. Introduction

The fabrication of self-organized nano-structures and nano-patterns has attracted much attention due to their technological impacts as well as the scientific interests to self-organization. Therefore, various synthesis processes have been reported. One of the highly promising processes to form self-organized nano-structures is a very simple electrochemical anodization. A well-established example of nano-structures produced by anodization is highly ordered nanoporous oxide layers on Al\textsuperscript{1,2}. Recently the formation of self-organized anodic nanoporous or nanotubular oxide layers has been reported on the other metals such as Ti\textsuperscript{3–8}, Zr\textsuperscript{9,10}, Hf\textsuperscript{11}, Nb\textsuperscript{12,13}, Ta\textsuperscript{14,15} and W\textsuperscript{16}. In particular TiO\textsubscript{2} nanotubular layer has been extensively studied owing to a wide range of applications of TiO\textsubscript{2}. For examples, TiO\textsubscript{2} nanotubular layers have been applied as photocatalyst\textsuperscript{17–19}, dye-sensitized solar cell\textsuperscript{20,21}, other functional and biomedical devices\textsuperscript{22–24}. Among the applications photocatalyst is one of the most examined applications of TiO\textsubscript{2} nanotubular layer. In order to enhance the photocatalytic efficiency of TiO\textsubscript{2} nanotubular oxide layers several surface modifications have been proposed; the decoration with metal or other semiconductor particles by various methods such as photoreduction, sputter deposition and wet chemical precipitation\textsuperscript{25–27}. Other unique route for the modification of TiO\textsubscript{2} nanotubular layer is alloy anodization. Paramasivam et al. reported that highly ordered nanoporous oxide layers containing WO\textsubscript{3} prepared by anodization of Ti-W alloys showed higher photocatalytic activity compared to bare TiO\textsubscript{2} nanotubular layers\textsuperscript{28}. This clearly indicates that the photocatalytic activity of TiO\textsubscript{2} nanotubular layer can be tuned by alloy anodization. Therefore, other elements that can improve the photocatalytic activity of TiO\textsubscript{2} are expected to be examined. Fe is the one of the candidates as it has been reported that porous oxide layers are formed on Fe surface by anodization and furthermore its oxides exhibit photocatalytic activity in visible light region, different from TiO\textsubscript{2}\textsuperscript{29,30}.

The present work reports the formation of nano-structured oxide layers by anodization of Ti-Fe alloy with Fe contents and especially addresses how substrate composition and anodization conditions affect the morphology of anodic oxide layers.

2. Experimental

Materials examined were Ti-x at% Fe alloys (x = 10, 50 and 70). The Ti-Fe alloys were prepared by melting high purity Ti and Fe sheets in an arc melting furnace. Specimens were cut with a dimension of 15 x 15 x 3 mm\textsuperscript{3} from the alloy ingots by spark machining. As it was reported that anodization of binary phase alloys such as Ti6Al4V and Ti6Al17Nb resulted in the inhomogeneous growth of oxide layers due to the selective dissolution of a less stable phase or different reaction rates depending on the phases\textsuperscript{31}, some of the specimens were homogenized at 1273 K for 24 h and then water-quenched. Prior to anodization all specimens were mirror-finished, followed by cleaning in ultra-sonic bath of acetone, methanol and deionized water, successively. The electrochemical cell used for anodization consisted of a two-electrode configuration with a platinum plate as a counter electrode. The specimens were pressed against an O-ring in the electrochemical cell, leaving the area of 0.785 cm\textsuperscript{2} exposed to an electrolyte. The electrolyte used in the present work was an ethylene glycol containing 0.05 mol L\textsuperscript{−1} NH\textsubscript{4}F and 1.1 mol L\textsuperscript{−1} H\textsubscript{2}O. For anodization voltage between the electrodes in anodic oxide layers increased from 0 V to a desired voltage with the voltage ramp rate of 1 Vs\textsuperscript{−1} and then was kept at the voltage for various anodization times. After the anodization the specimens were rinsed with ethanol and then dried with N\textsubscript{2} stream.

Morphological characterization of resulting oxide layers was performed using a field-emission scanning electron microscope (FE-SEM, JEOL JSM-7001FA). Cross-sectional SEM images were taken from mechanically scratched samples, where a partial lift-off of oxide layers occurred.
3. Results and Discussion

From a set of preliminary anodization experiments, an ethylene glycol containing 0.05 mol L$^{-1}$ NH$_4$F and 1.1 mol L$^{-1}$ H$_2$O was determined as anodization electrolyte for the Ti-Fe alloys. Figure 1 shows current-voltage curves from 0 V to 30 V and subsequent current-time curves for the Ti-Fe alloys at 30 V for 3 h in the electrolyte. The one obtained for pure Ti was also included for comparison. For pure Ti and the Ti-10 at% Fe alloy, the current density steeply increases until the applied voltage reaches 10 V and then presents gradual increase while the current density for the Ti-50 at% Fe and Ti-70 at% Fe alloys significantly increases until the anodization voltage of 30 V. After switching to the constant voltage of 30 V, the current-time curves of all substrates exhibit drastic decrease in the very early stage, then slight increase once and finally gradual decrease to a steady state value. The steady state current obtained for the Ti-10 at% Fe and Ti-50 at% Fe alloys are similar to that for pure Ti. However, the one obtained for the Ti-70 at% Fe alloy is clearly much higher compared to those for pure Ti and the Ti-Fe alloys with lower Fe content.

Figures 2 and 3 show top-surface and cross-sectional images of resulting oxide layers, respectively. Nanotubular oxide layers were grown on pure Ti, Ti-10 at% Fe and Ti-70 at% Fe alloy although the initiation layers$^{32)}$ still remain on the surfaces of pure Ti and Ti-10 at% Fe even after anodization for 3 h. The initiation layers are formed in the early stage of anodization and nanotubular oxides are grown underneath the initiation layers. The details are described later. On the other hand, it is obvious from Figs. 2(c) and 3(c) that totally different morphology is observed for the oxide layer formed on the Ti-50 at% Fe alloy. Namely, an irregular-shaped porous oxide layer is grown on the alloy. Furthermore the thickness of the oxide layer on the Ti-50 at% Fe alloy is quite thinner compared to those for pure Ti, the Ti-10 at% Fe and Ti-70 at% Fe alloys. These indicate that the morphology of anodic oxide layer depends on the chemical composition of substrate alloy when the Ti-Fe alloys are anodized at 30 V. The effect of applied voltage on the morphology of anodic oxide layer was also examined in the present work. Figure 4 presents SEM images of anodic oxide layers formed on pure Ti and the Ti-Fe alloys at 50 V. As apparent from the images, nanotubular oxide layers are formed on pure Ti and the Ti-10 at% Fe alloy at 50 V as similar to 30 V whereas irregular-shaped porous oxide layers are grown on the Ti-50 at% Fe and Ti-70 at% Fe alloys. However, the effect of applied voltage on the morphology of anodic oxide layer observed for the substrates anodized at 10 V is different compared to those presented at the higher applied voltages. The morphology of anodic oxide layers formed at 10 V on the Ti-Fe alloys is presented in Fig. 5. It is clear that the anodic oxide layers exhibit nanotubular structure on all substrates at this voltage. Therefore it is found that nanotubular oxide layers are formed on pure Ti and the Ti-10 at% Fe alloy at various voltages ranging from 10 V to 50 V. For the Ti-50 at% Fe and Ti-70 at% Fe alloy, on the other hand, significant changes in the oxide morphology are recognized, that is, the morphological change from a nanotubular oxide layer to an irregular-shaped porous oxide layer is observed.

![Fig. 1](image1.png) Current transients during the anodization of pure Ti, Ti-10 at% Fe, Ti-50 at% Fe and Ti-70 at% Fe alloys at 30 V in the ethylene glycol containing 0.05 mol L$^{-1}$ NH$_4$F and 1.1 mol L$^{-1}$ H$_2$O. The arrows indicate the current density defined as the initial currents.

![Fig. 2](image2.png) Top-surface SEM images of anodic oxide layers formed on (a) pure Ti, (b) Ti-10 at% Fe, (c) Ti-50 at% Fe and (d) Ti-70 at% Fe alloys at 30 V for 3 h in the ethylene glycol containing 0.05 mol L$^{-1}$ NH$_4$F and 1.1 mol L$^{-1}$ H$_2$O.

![Fig. 3](image3.png) Cross-sectional SEM images of anodic oxide layers formed on (a) pure Ti, (b) Ti-10 at% Fe, (c) Ti-50 at% Fe and (d) Ti-70 at% Fe alloys at 30 V for 3 h in the ethylene glycol containing 0.05 mol L$^{-1}$ NH$_4$F and 1.1 mol L$^{-1}$ H$_2$O.
bular structure to an irregular-shaped porous structure occurs although the threshold voltage for the change is different depending on Fe content in the alloys.

Similar morphological change was observed on Ti-Ni alloys where the change in the morphology of oxide layer from nanotubular to irregular-shaped porous structures occurred as the anodization time was increased. Therefore, it may be considered that the anodization time of 3 h is long enough to reach the situation where irregular-shaped porous oxide layers are grown on the Ti-50 at% Fe alloy at 30 V whereas longer anodization time than 3 h is required to grow irregular-shaped porous structures on the alloy at 10 V. In order to get the effect of anodization time on the morphology of anodic oxide layer, anodization experiments were carried out for different anodization times. Figures 6 (a) and (b) show top-surface and cross-sectional SEM images of the oxide layer formed on Ti-50 at% Fe alloy at 10 V for 18 h, respectively. A nanotubular oxide layer is clearly confirmed on the alloy after anodization at 10 V for 18 h. On the other hand, the morphology of the anodic oxide layer after anodization at 30 V for 1 h exhibits irregular-shaped porous structure as shown in
Figs. 6 (c) and (d). Therefore, it is found that the morphological change is not induced by anodization time in the case of Ti-Fe alloy.

The results presented above were obtained by potentiostatic anodization where anodic oxide layers were grown on the Ti-Fe alloys at constant voltage. In order to examine the effect of current density generated during anodization on the morphology of anodic oxide layers, galvanostatic anodization of the Ti-Fe alloys was also performed, that is, constant current was applied. Figure 7 shows SEM images of anodic oxide layers formed on the Ti-50 at% Fe alloy at different constant current densities for 3 h. It is clear that the anodic oxide layers formed at the smaller current densities such as 1.2 A m$^{-2}$ and 3.5 A m$^{-2}$ exhibit nanotubular structures while irregular-shaped porous structure is observed for the oxide layer formed at the larger current density as 6.3 A m$^{-2}$ as shown in Fig. 7(f). This result indicates that the current density can be responsible for the formation of the irregular-shaped porous oxide layers. Therefore, the morphology of anodic oxide layers is discussed in terms of current density. As presented in Fig. 1, the current transient is almost similar for all substrates, that is, the current density generated at constant voltage significantly decrease in the early stage, slightly increases and then gradually decreases to a steady state value. It was reported that the current transient during anodization is strongly related to the formation and growth of nanotubular oxide layers$^{34}$. In the early stage, a compact oxide layer is formed and grown by a classic high-field model$^{35}$. The current exhibits significant decay due to increasing thickness of the compact oxide layer. In the next stage, random nanoscopic pores are initiated due to the chemical dissolution of the formed compact oxide layer by fluoride ions and penetrate the compact oxide layer, resulting in the formation of nanotubes underneath the compact oxide layer. This leads to the increase of the current as the active surface area increases. The penetrated compact oxide layers sometimes remain after anodization as initiation layer$^{32}$. In the last stage, a steady-state situation is established where a nanotubular oxide layer grows with a speed that is proportional to the current. The growth may be influenced by the diffusion of chemical species within nanotubes. Therefore, the current slightly decreases with time due to increasing diffusion length. From the consideration on the growth mechanism of nanotubular oxide layer, it can be deduced that the initiation of nanoscopic pores and the steady-state growth process are the factors that affect the morphology of anodic oxide layer. Therefore, the current density just before the increase is defined as the initial current and pointed by the arrows in Fig. 1. The current can affect the initiation of nanoscopic pores. On the other hand the current density obtained just before the termination of anodization is defined as the final current that reflects the steady-state growth. Figure 8 summarizes the morphology of anodic oxide layers formed on the Ti-50 at% Fe alloy under all anodization con-
of the oxide layers formed on the Ti-50 at% Fe alloy by the two-step galvanostatic anodization where the larger current density first and then the smaller current density are applied. It is clear that the anodic oxide layer exhibits irregular-shaped porous structure. On the other hand, when the constant currents are applied in the reverse procedure, the formation of nanotubes is confirmed as shown in Fig. 9(b). From these results it is concluded that the formation of the irregular-shaped porous oxide layers at higher voltage is attributed to the generation of large current in the initial stage of anodization, in other words, it can be required to suppress initial current density during anodization in order to form nanotubular oxide layers on the Ti-Fe alloys.

4. Conclusions

In the present work we examined the morphology of anodic oxide layers on the Ti-Fe alloys in an ethylene glycol electrolyte containing NH$_4$F and H$_2$O. On pure Ti and the Ti-10 at% Fe alloy, nanotubular oxide layers were formed at all voltages examined. In the case of the Ti-50 at% Fe, a nanotubular oxide layer was grown only at 10 V. At the higher voltages as 30 V and 50 V, on the other hand, irregular-shaped porous structures were obtained; the morphological change from nanotubular to irregular-shaped porous structures was observed on the Ti-50 at% Fe alloy. Similar morphological change occurred also on the Ti-70 at% Fe, but the threshold voltage was higher compared to the Ti-50 at% Fe alloy. That is, the morphology of anodic oxide layers was affected by substrate composition as well as anodization voltage. The morphological change was related to the current density in the early stage of anodization and lower initial current density could be required to form nanotubular oxide layers on the Ti-Fe alloys.

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