

Preparation of Anatase Film by the Solution Process

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Bioactive ceramic coating was formed on a titanium substrate hydrothermally. An anatase film was formed on a titanium substrate through two solution processes. The titanium substrate was first treated in potassium hydroxide solution ($1.8 \text{ mol}\cdot\text{dm}^{-3}$) at $40\text{-}150^\circ\text{C}$ for 1-24 h to deposit a potassium titanate layer on it. At the second process, the potassium titanate layer was heated in the dilute hydrochloric acid solution over 120°C , then the potassium titanate decomposed and anatase formed on the surface of the substrate. The fine crystals of hydroxyapatite precipitated on the coated surface, after the soaking in the simulated body fluid for 7 days at 37°C . The potassium titanate was not well crystallized, and thickness of the layer increased with the temperature and with the duration of the first process. The thickness of the anatase film was less than 200 nm, when the temperature of the first process was less than 60°C , and the roughness of the film also decreased, the enough adhesion between the substrate and the coating was achieved.

Key words: anatase, hydrothermal treatment, potassium titanate, simulated body fluid, hydroxyapatite

1. INTRODUCTION

Titanium and titanium alloys were used for repairing the living bones and their surface was modified several method to form titanium oxide or other coating layer. For example, Hamada et al.¹⁾ reported that the hydrothermal modification of titanium surface in calcium oxide solution enhanced the precipitation of apatite in soaking Hanks' solution at 37°C . Wen et al.²⁾ treated Ti6Al4V alloy in sodium hydroxide (NaOH) solution at 140°C to form a titanium oxide layer on the surface. After immersion in fast calcification solution (FCS) or Hanks' balanced salt solution (HBSS) at 37°C , a calcium phosphate was precipitated on the surface. Kim et al.³⁾ reported that after the treatment in 5 M NaOH solution at 24 h and heat treatment in air at 600°C , an amorphous sodium titanate layer was formed on the surface of pure titanium. The surface of the treated titanium formed an apatite surface layer in simulated body fluid⁴⁾ (SBF). Wu et al.⁵⁾ treated titanium in hydrogen peroxide solution and heated it at 300°C . A porous anatase film was formed on the titanium. They also reported⁶⁾ that the crystallization of anatase at 80°C and the apatite formation on the surface in SBF.

In the previous study⁷⁾, we formed porous anatase layer on a titanium substrate using inexpensive materials by a hydrothermal method. First of this process, a calcium titanate layer was formed on a titanium substrate. Then the calcium titanate coating was dissolved in HCl solution at 180°C , and anatase was formed. Though the adhesion between the anatase layer and the substrate improved by using thin calcium titanate coating to form anatase layer, a part of layer fractured after peeling test because of its roughness.

In this study, we synthesized potassium titanate film with smaller roughness in order to form a smooth thin anatase layer with good adhesion to the substrate.

2. EXPERIMENTAL

The solution of potassium hydroxide (KOH; Kanto Chemical co., Reagent Grade) was dissolved in distilled water to prepare the stock solution. As the first process, a Ti plate (Nilaco Co., $10 \times 40 \times 0.05 \text{ mm}^3$) as a substrate was reacted with the KOH solution in a Teflon-lined stainless-steel autoclave at $40\text{-}150^\circ\text{C}$ for 1-24 h. The concentration of KOH was $1.8 \text{ mol}\cdot\text{dm}^{-3}$. The reacted substrates were rinsed in distilled water using an ultrasonic wave and dried at 70°C for 24 h.

The reacted substrates were treated in aqueous solutions of hydrochloric acid (HCl; Sankyo Chemical co., Reagent Grade) at 180°C for 24 h to form anatase (acid treatment). The pH of the treated solution (at 20°C) was adjusted to 2.0. The substrates were weighed before and after each treatment. The films were analyzed by the thin film X-ray diffractometry (TF-XRD: Philips X'Pert-MPD-PW3050) using Cu radiation to identify the crystalline phases, and the surface morphology of the film was observed by scanning electron microscopy (SEM: JEOL JSM-5310).

The thickness of the film was estimated by X-ray induced photoelectron spectroscopy (ESCA: PerkinElmer, Inc. model 5500 MT) and the roughness of the film was measured by atomic force microscopy (AFM: Digital Instruments, Inc.). The adhesion between the film and the substrate was tested using the adhesive tape (Nichiban. co., Ltd., No.405, $4.2 \text{ N}/10\text{mm}$). The samples were cut into the size $10 \times 20 \text{ mm}^2$ and the adhesion tape

was adhered on it carefully not to put the air between the tape and the surface of the film. In order to fix the tape on the surface of the sample, the tape was rubbed using a plastic eraser. The tape was torn off at one time at the uniform angle as much as possible. The peeling of the film was judged by the visual observation.

The films after the acid treatment were cut into $10 \times 20 \text{ mm}^2$ sections, and soaked in 20 cm^3 of SBF⁴⁾ at 37°C for 7 days. The ion concentrations and pH of the solution were almost equal to those of human blood plasma. After soaked in SBF, the sample was observed by SEM and the change in weight was measured.

3. RESULTS AND DISCUSSION

3.1 Deposition of potassium titanate

Figure 1 shows the change in the weight of the titanium substrate reacted in $1.8 \text{ mol}\cdot\text{dm}^{-3}$ KOH solution at 150°C for various durations.

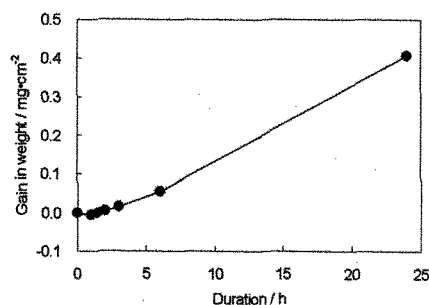


Fig. 1. Change in the weight of titanium substrate reacted in KOH solution at 150°C with increasing reaction duration.

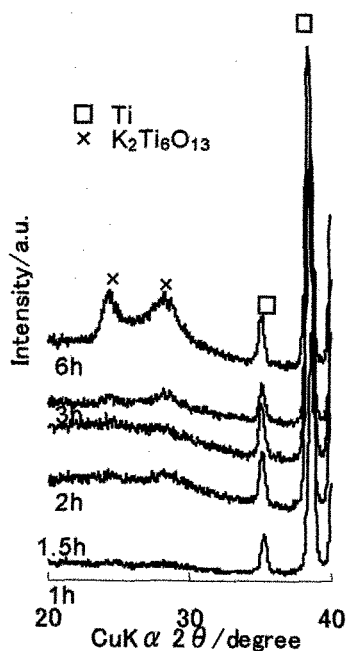


Fig. 2. TF-XRD patterns of Ti substrate reacted in KOH solution at 150°C .

The TF-XRD patterns of the substrate after reacted in the KOH solution is shown in Fig. 2. The weight of the substrate decreased till 1h, and then increased with duration gradually. A potassium titanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$) was formed on the substrates reacted over 1.5 h. The titanium substrate was dissolved and the broad peak in the TF-XRD pattern by the potassium titanate was slightly recognized, when the substrate reacted in KOH solution for 1 h.

The SEM photographs of the surface of the reacted substrates are shown in Fig. 3. The fibrous structure was observed, even after 1 h reaction. The amount of the fibrous material increased with the reaction duration. Table I shows the chemical composition of the reacted surface by ESCA. The atomic ratio of K/Ti at 6h was 0.34 which was nearly equal to that of $\text{K}_2\text{Ti}_6\text{O}_{13}$ (0.33), though the ratio at 2 h was 0.17. It seemed that the titanium substrate was dissolved and the amorphous titanium oxide was formed on the surface firstly, and the potassium titanate was crystallized.

Table I. Chemical composition of the surface of the film

Duration / h	O	Ti	K	K/Ti	C
2	44.79	18.21	3.07	0.17	31.39
6	42.65	16.26	5.48	0.34	33.27

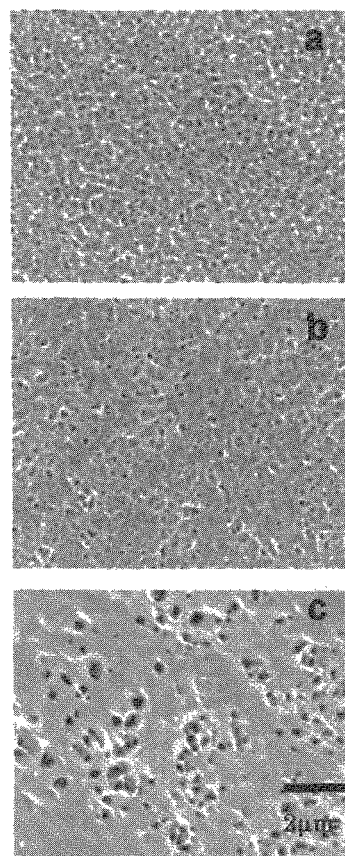


Fig. 3. SEM photographs of surface of the substrate treated in KOH solution at 150°C for 1 h (a), 2 h (b) and 6 h (c).

3.2 Formation of anatase by the acid treatment

An anatase was formed after the acid treatment (pH 2.0) of the potassium titanate layers at 180°C for 24 h, regardless of the synthesis duration of the potassium titanate, though a rutile, the other crystalline titanium oxide, was also formed. Then the effect on the formed phases of the duration and the temperature of the acid treatment was examined. In a following experiment, the potassium titanate layer was formed at 150 °C for 2 h in 1.8 mol dm⁻³ KOH solution. The change in the TF-XRD patterns of titanium oxide layers after the acid treatment with various durations at 180°C, and various temperatures for 3 h are shown in Figs 4 and 5, respectively. Anatase was formed even when the sample was treated in HCl for 1h. However rutile did not form till 3 h. The formation of anatase was observed over 100°C for 3 h (Fig. 5). Yanagisawa et al.⁸⁾ reported that the crystallization of anatase was enhanced by the existence of the chloride ions and the high pH. In the condition of this study, it was easy to form anatase rather than rutile, in spite of the low pH. The potassium titanate slightly remained after the treatment at 80°C.

Table II shows the chemical composition of the surface layer treated by HCl at various temperatures for 3 h. The potassium was existed at the surface treated at 80°C and was not dissolved from the surface. On the contrary, potassium was dissolved over 100°C. The SEM photographs of the surface of the layer after the acid treatment are shown in Fig.6. The fibrous microstructure was not observed over 120°C, though such structure was remained at 100°C and under.

Table II. Chemical composition of the surface layer treated by HCl for 2 h

Temp./°C	O	Ti	K	K/Ti	C
80	50.75	21.24	4.07	0.19	24.62
100	51.72	22.62	0	-	25.65
180	50.72	21.36	0	-	27.92

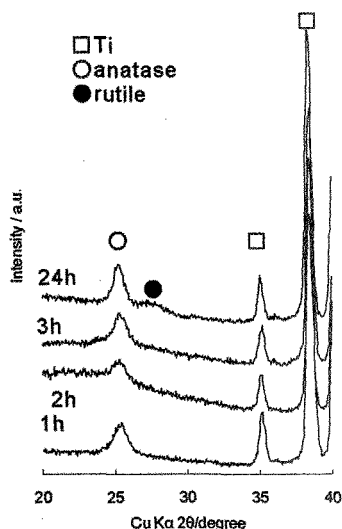


Fig.4. TF-XRD patterns of the titanium oxide layer formed after the HCl treatment for various durations at 180°C.

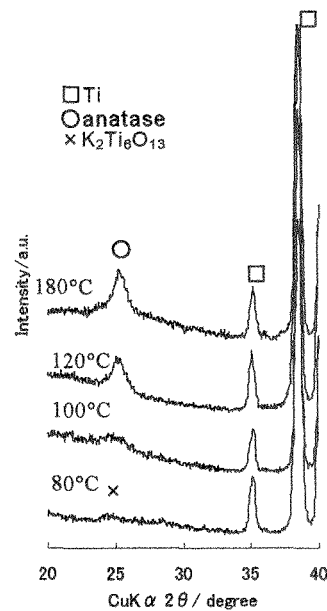


Fig.5. TF-XRD patterns of the titanium oxide layer formed after the HCl treatment for 3 h at various temperatures.

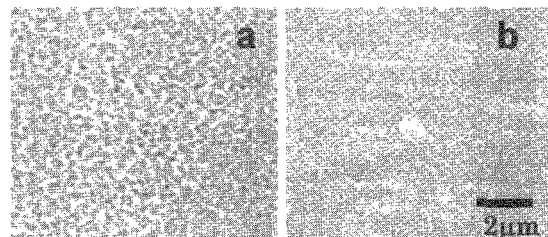


Fig.6. SEM photographs of the potassium titanate layer formed by the acid treatment for 2 h at 100°C (a) and 120°C (b).

3.3 The roughness and the thickness of anatase film

The adhesion between the substrate and anatase layer was examined by the adhesive tape (4.2 N/ 10mm). Figure 7 shows the effect of the synthesis conditions of the potassium titanate layer on the adhesion between the substrate and the anatase layer after the HCl treatment at 180°C for 3 h. The synthesis conditions of the potassium titanate that the anatase layer was not peeled off from the substrate are shown in open circles. The cross means that the layer was peeled off or broken. The anatase layer did not peel off, when the synthesis duration of potassium titanate was 1 h or less at 150°C, or when the synthesis temperature was lower than 60°C for 2h. The adhesion of the layer was enhanced, when the synthesis duration was short and the synthesis temperature was low.

The thickness of the titanium oxide layer was more than 240 nm, when the potassium titanate layer was synthesized at 150°C before the acid treatment. On the other hand, the thicknesses of the titanium oxide layer formed from the potassium titanate synthesized at 80 and 60°C were 210 and 150nm, respectively. The thickness of the potassium titanate layer increased with the reaction time as shown in Fig.1, and the thickness

of the titanium oxide layer after the acid treatment might be also increased with the thickness of the potassium titanate. In the condition in which the thickness of the titanium oxide was thin, the adhesion was high.

The surface roughness of the substrate and of the anatase film was measured (Fig.8). The roughness of the titanium substrate was almost 50nm. The surface roughness of the anatase film obtained from the potassium titanate synthesized at 150 and 60°C were almost 300 nm and 50 nm, respectively. The thicker the potassium titanate film, the surface roughness of the anatase layer was increased, and the film became easy to peel off or to be broken. During the acid treatment, almost all the potassium dissolved and porous anatase layer was formed. In order to obtain the adhesive anatase layer, thin film with smooth surface was desirable.

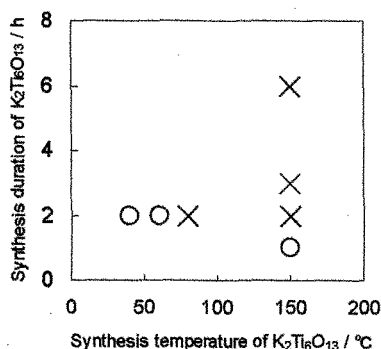


Fig.7. Effect of the synthesis condition of potassium titanate on the adhesion between the anatase film and the substrate. The potassium titanate was treated in HCl at 180°C for 3h.

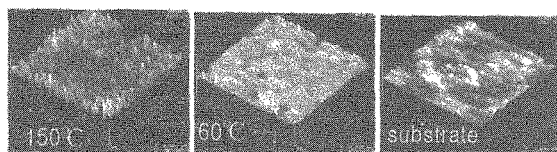
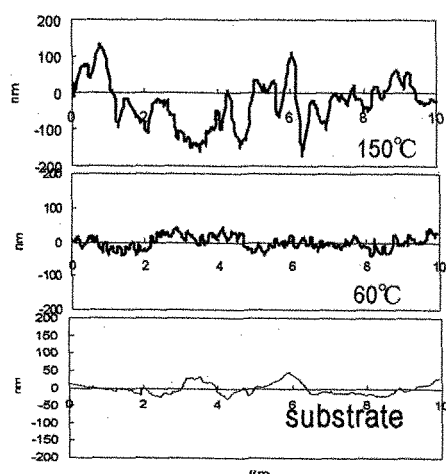


Fig.8. Surface roughness of the substrate and anatase films obtained from the potassium titanate synthesized at 150°C and 60°C

3.4 Precipitation of HAP on the anatase film in SBF

The anatase film was soaked in the SBF at 37°C for 7days. The surface of the film was covered with HAP crystals (Fig. 9). The amounts of the deposited HAP on the anatase layer with different thickness of anatase were almost equal. The thickness of the anatase film did not influence the deposition of HAP from the SBF.

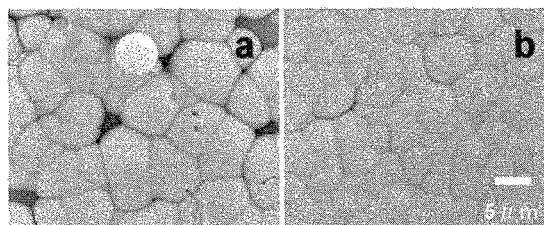


Fig.9. SEM photographs of the surfaces of the anatase films formed after the acid treatment of the potassium titanate layer synthesized for 2 h at 150°C (a) and 60°C (b), after soaked in SBF at 37°C for 7days.

4. CONCLUSION

Anatase film was formed by the hydrothermal treatment of the potassium titanate film. The potassium titanate was decomposed in the hydrothermal HCl solution, and anatase crystallized. The temperature of hydrothermal treatment over 120 °C was required to form anatase, though the long treatment led the formation of rutile.

The temperature and the duration of potassium titanate synthesis had to be lowered and shortened, respectively, in order to obtain the thin and relatively smooth anatase film and to enhance the adhesion to the substrate. The HAP crystals were deposited on the anatase films after they were soaked in the SBF.

Acknowledgements

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