

Apatite Formation on Hydrochloric Acid Treated Titania Thin Film Synthesized from Aqueous Solution

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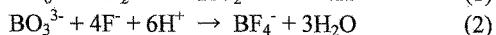
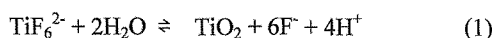
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We have already reported that titania thin film synthesized on organic polymers from aqueous solution formed apatite layer on its surface when soaked in a solution with ion concentrations 1.5 times those of simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma. When the apatite forming ability of titania thin film is advanced further, bioactive materials with various mechanical properties can be developed. In this study, we have treated titania thin film with hydrochloric acid and examined apatite formation on its surface when it was soaked in SBF. Titania thin film was synthesized on poly(ethylene terephthalate) substrate through a hydrolysis reaction of titanium fluoro-complex in an aqueous solution. And then the substrate was treated with hydrochloric acid. The treated substrate was soaked in SBF. As the result, when titania thin film was treated with $0.1 \text{ mol} \cdot \text{dm}^{-3}$ HCl for 7d, apatite was formed on its surface after 5 d, and the substrate was almost completely covered with apatite layer after 14d. This method is promising for developing hard and soft tissue implants with various mechanical properties as well as high bioactivity and bioaffinity.

Key words: Apatite, Titania, Hydrochloric Acid, Simulated Body Fluid, Synthesis from Aqueous Solution

1. INTRODUCTION

Previously, we have presented that titania (TiO_2) thin film can be formed from aqueous solution at ordinary temperature and ordinary pressure [1-3]. The reaction formula is as follows.



It is considered that the chemical equilibrium between hexafluorotitanate ion and TiO_2 holds as in reaction (1). When borate ion is added, fluoride ion is consumed by reaction (2), then the chemical equilibrium in reaction (1) shifts from left to right to increase fluoride ions, resulting in the formation of titania. This method is advantageous because no vacuum, no high temperature and no expensive apparatus will be required, and substrates, even those with wide areas and/or complicated shapes, are available. Previously, we have presented that the titania thin film formed on titanium metal and glass substrates by this method has an apatite-forming ability in simulated body fluid: SBF, which have nearly equal concentrations of inorganic ions to those of human blood plasma (Na^+ 142.0, K^+ 5.0, Ca^{2+} 2.5, Mg^{2+} 1.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0 and SO_4^{2-} 0.5 $\text{mmol} \cdot \text{dm}^{-3}$, pH 7.4) and considered that Ti-OH groups induce the nucleation of apatite [4,5]. When titania thin film is formed on wide variety of materials, especially low heat resistant materials such as organic polymers, by using this method, and has an apatite-forming ability, bioactive materials with various mechanical properties can be developed. We have already reported that titania thin film synthesized by using this method have apatite forming ability in a simulated body fluid with ion concentrations nearly 1.5 times those of human blood plasma: 1.5SBF (Na^+ 213.0, K^+ 7.5, Ca^{2+} 3.8, Mg^{2+} 2.3, Cl^- 221.7, HCO_3^- 6.3, HPO_4^{2-}

1.5 and SO_4^{2-} 0.8 $\text{mmol} \cdot \text{dm}^{-3}$, pH 7.4), however, apatite forming ability was not observed when soaked in SBF [6]. On the other hand, J.G. Yu et al. have reported that the Ti-OH content increases after hydrochloric acid treatment on TiO_2 thin film formed by sol-gel method [7]. In our present study, titania thin film formed on organic polymer by this method was treated with hydrochloric acid and the apatite-forming ability was investigated.

2. EXPERIMENTAL

2.1 Formation of TiO_2 thin film

Poly(ethylene terephthalate) [PET; Tsutsunaka Plastic Industry Co., Ltd.], $10 \times 10 \times 1 \text{ mm}^3$ in size, were used as substrates. The substrates were soaked in suspension of anatase-type titania nano particles as seed crystals for 20 min. Ammonium hexafluorotitanate [$(\text{NH}_4)_2\text{TiF}_6$; Morita Chemical Industries Co., Ltd.] and boron trioxide [B_2O_3 ; Wako Pure Chemical Industries, Ltd.] were respectively dissolved in distilled water to give the solutions with concentrations of 2.5 $\text{mmol} \cdot \text{dm}^{-3}$ and 240 $\text{mmol} \cdot \text{dm}^{-3}$. Then thus prepared $(\text{NH}_4)_2\text{TiF}_6$ solution and B_2O_3 solution were mixed together at 1 : 3 volume ratio. The final concentrations were 0.625 $\text{mmol} \cdot \text{dm}^{-3}$ and 180 $\text{mmol} \cdot \text{dm}^{-3}$, respectively. After that the substrate was suspended in 30 ml of the mixed solution in a plastic bottle and the bottle was placed in an incubator at 40°C for 24 h. After soaking, the substrate was washed with distilled water and dried at room temperature.

2.3 Treatment with HCl

1 $\text{mol} \cdot \text{dm}^{-3}$ hydrochloric acid [1 $\text{mol} \cdot \text{dm}^{-3}$ HCl; Hayashi Pure Chemical Ind., Ltd.] was used as received or diluted to 0.1 $\text{mol} \cdot \text{dm}^{-3}$. TiO_2 thin film synthesized on the substrate was treated at 60°C with 1 $\text{mol} \cdot \text{dm}^{-3}$ HCl for 1h or 1d or 0.1 $\text{mol} \cdot \text{dm}^{-3}$ HCl for 7d or 14d. After soaking, the substrate was washed with distilled water.

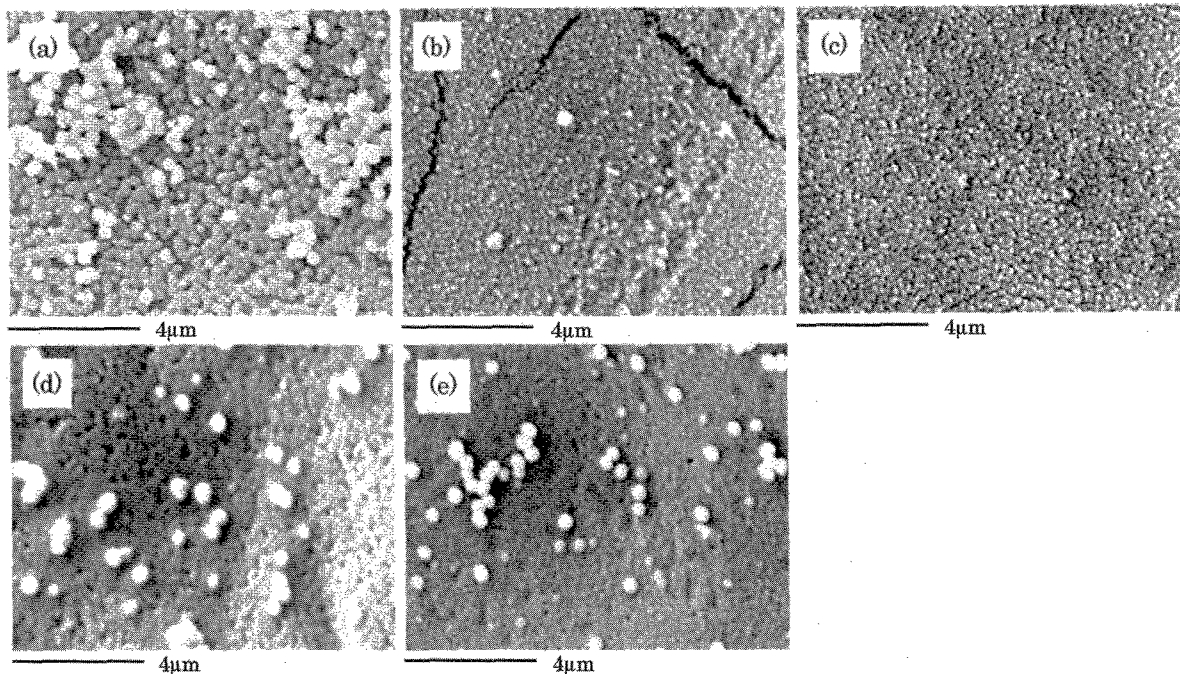


Fig.1 SEM micrographs of the surfaces of the PET substrates. (a)TiO₂ thin film synthesized from aqueous solution, treated with 1 mol·dm⁻³ HCl for (b)1h and (c)1d and treated with 0.1 mol·dm⁻³ HCl for (d)7d and (e)14d.

2.4 Evaluation of apatite-forming ability

SBF was prepared with following reagent grade chemicals: sodium chloride [NaCl; Wako], sodium hydrogen carbonate [NaHCO₃; Hayashi], potassium chloride [KCl; Hayashi], dipotassium hydrogen phosphate trihydrate [K₂HPO₄·3H₂O; Takeuchi Yakuhin Co., Ltd.], magnesium chloride hexahydrate [MgCl₂·6H₂O; Hayashi], calcium chloride anhydrous [CaCl₂; Hayashi] and sodium sulfate anhydrous [Na₂SO₄; Hayashi]. These chemicals were dissolved into ion-exchanged and distilled water in polyethylene beaker and the solution was buffered at pH 7.40 with 1 mol·dm⁻³ HCl and 2-amino-2-hydroxymethyl-1,3-propanediol [C₄H₁₁

NO₃; Hayashi] at 36.5°C. The substrate after treated with HCl was soaked in SBF for 3d, 5d, 7d or 14d. After the soaking, the substrate was washed with distilled water.

2.5 Analysis of surface of the substrate

Analysis of surface of the substrate was carried out with thin film X-ray diffractometry [TF-XRD; Model Rint 2500, Rigaku Co., Ltd., Japan], scanning electron microscopy [SEM; ESEM-2700, Nikon Corporation] and energy dispersive X-ray analysis for elemental identification [EDX; Model DX-4, Edax International Inc.]. All of the substrates for SEM analysis were coated with Au.

3 RESULTS AND DISCUSSION

3.1 Formation of TiO₂ thin film and the results of treatment with HCl

Fig.1 and Fig.2 show SEM micrographs and results of EDX element analysis of TiO₂ thin film formed from aqueous solution, and results of HCl treatment, respectively. After soaking in the (NH₄)₂TiF₆ and B₂O₃ mixed solution, formation of TiO₂ thin film on the entire surface of the substrate was observed by visual observation. The surfaces of the substrates treated with HCl of 1 mol·dm⁻³ were seemed to be more rough than those of 0.1 mol·dm⁻³. When the substrate was treated with HCl of 1 mol·dm⁻³, Ti peak was still visible in EDX spectra after 1h, but was no longer visible after 1d. This implies that almost all TiO₂ thin film dissolved after 1d treatment in HCl of 1 mol·dm⁻³ treatment. On the other hand, when the substrate was treated with HCl of 0.1 mol·dm⁻³, Ti peak was still visible in EDX spectra after 14d.

3.2 Evaluation of apatite-forming ability

After soaking in SBF for the various periods, apatite

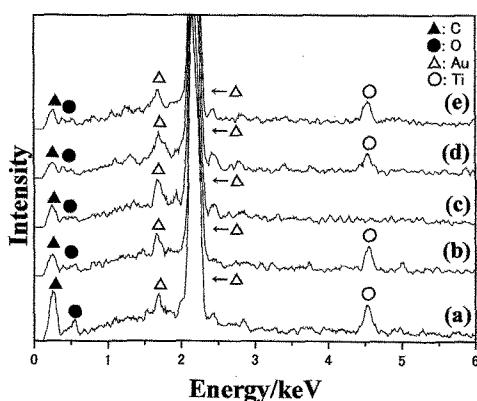


Fig.2 EDX spectra of the surfaces of the PET substrates. (a)TiO₂ thin film synthesized from aqueous solution, treated with 1 mol·dm⁻³ HCl for (b)1h and (c)1d and treated with 0.1 mol·dm⁻³ HCl for (d)7d and (e)14d.

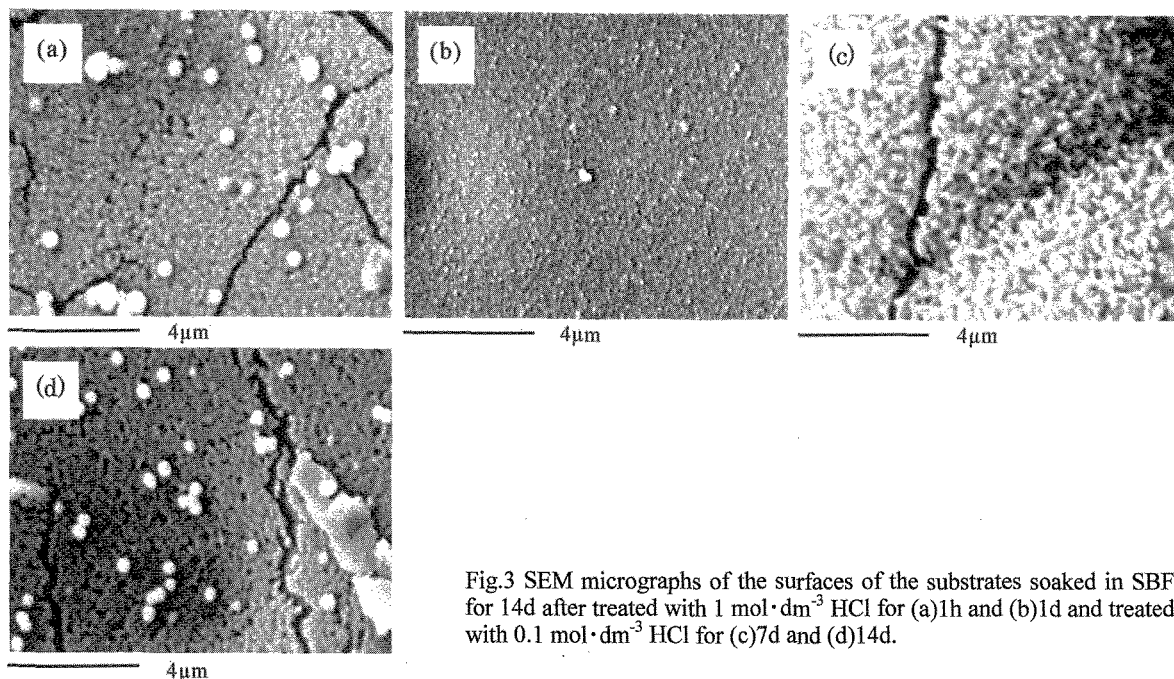


Fig.3 SEM micrographs of the surfaces of the substrates soaked in SBF for 14d after treated with 1 mol·dm⁻³ HCl for (a)1h and (b)1d and treated with 0.1 mol·dm⁻³ HCl for (c)7d and (d)14d.

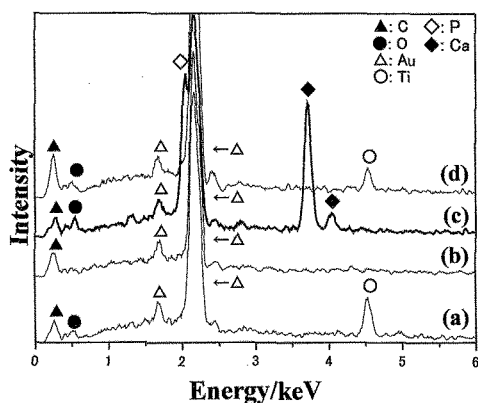


Fig.4 EDX spectra of the surfaces of TiO₂ thin films soaked in SBF for 14d after treated with 1 mol·dm⁻³ HCl for (a)1h and (b)1d and treated with 0.1 mol·dm⁻³ HCl for (c)7d and (d)14d.

was formed on the surface of TiO₂ thin film treated with 0.1 mol·dm⁻³ HCl for 7d. While under the other treatment conditions apatite was not formed on the thin films even after 14d soak. Fig.3 and Fig.4 show SEM micrographs and results of EDX element analysis of the surfaces treated with various conditions and then soaked in SBF for 14d. Comparing SEM micrographs of Fig.1 and Fig.3, remarkable change was observed on the surface of the substrate treated with 0.1 mol·dm⁻³ HCl for 7d. Also, comparing EDX spectra shown in Fig.2 and Fig.4, Ti peak in Fig.2(c) was disappeared and peaks of Ca and P were appeared (Fig.4(c)) by SBF soak for the same substrate. For other conditions of HCl treatment, no change was observed on the surface of the substrates by SBF soak. In Fig.5, TF-XRD patterns of the surface of the substrates treated with 0.1 mol·dm⁻³ HCl for 7d and then soaked in SBF for various periods are shown. An apatite peak appeared after 5d soak and intensities of apatite peaks increased with increasing

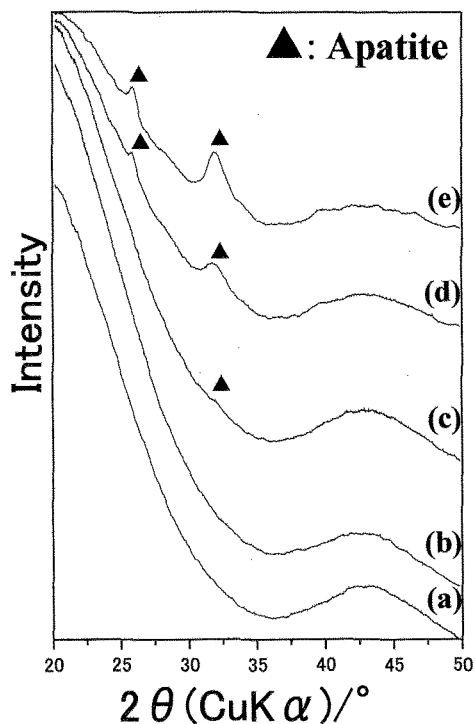


Fig.5 TF-XRD patterns of the surfaces of TiO₂ thin films treated with 0.1 mol·dm⁻³ HCl for 7d and then soaked in SBF for (a)0d, (b)3d, (c)5d, (d)7d and (e)14d.

soak time. In Fig.6, SEM micrographs for the same sample were shown. After 3d soak, small particles are formed on the surface of the substrate. By EDX analysis, P and Ca were detected for these particles. It's supposed that these small particles should be composed of apatite. Particles grew larger and connected to form thin film with the increase of soaking time. It is suggested that with HCl treatment on titania thin film the content of

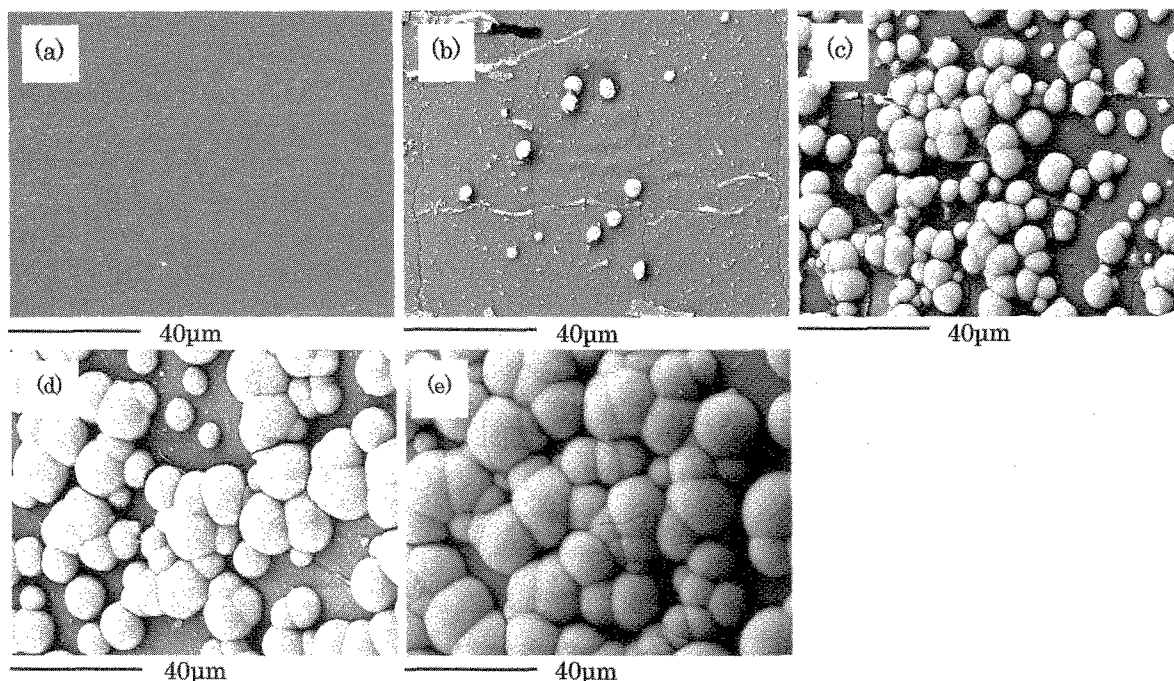


Fig.6 SEM micrographs of the surfaces of TiO_2 thin films treated with $0.1 \text{ mol} \cdot \text{dm}^{-3}$ HCl for 7d and then soaked in SBF for (a)0d, (b)3d, (c)5d, (d)7d and (e)14d.

Ti-OH groups increased, and which makes the surface active for apatite formation. When HCl content was higher or treatment time was longer, no apatite formation was observed. It is suggested that the excess HCl treatment induce dissolution of TiO_2 thin film and make reduction of Ti-OH amount.

4 CONCLUSIONS

Titania thin film was formed on poly(ethylene terephthalate) substrate by a hydrolysis reaction of titanium fluoro-complex in an aqueous solution. The substrates were treated with hydrochloric acid and, then, soaked in an aqueous solution with ion concentrations nearly those of human blood plasma. Apatite was formed on the substrate. This hydrochloric acid treatment will give good apatite forming ability to the surface of titania thin film formed on various materials. Bioactive materials with various mechanical properties can be developed by the present method.

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