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Research Article

Fabrication of Bioactive Apatite Nuclei Precipitated Titanium by Using Electromagnetic Induction Heating

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Abstract Many micro pores were formed on the surface of a titanium (Ti) plate by sulfuric acid treatment, then apatite nuclei were precipitated in the pores of the Ti plate by direct heating of the plate by using electromagnetic induction in a simulated body fluid (SBF). When the Ti plate was soaked in SBF, amorphous calcium phosphate thin film covered the whole surface within 6 h and it grew into hydroxyapatite within 12 h. The hydroxyapatite layer showed high adhesive strength to the Ti plate due to a mechanical interlocking effect between hydroxyapatite grown in the micro pores and the Ti plate.

Keywords titanium; apatite nuclei; bioactivity; electromagnetic induction heating; mechanical interlocking effect

1 Introduction

Titanium (Ti) is an excellent biomaterial with good mechanical property and bioaffinity. If bioactivity of Ti is further enhanced, the range of its application will be largely extended. When either pH or temperature of a simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma [2] is raised, fine particles of calcium phosphate are precipitated in the fluid. Previously, we found that the fine particles are very active for forming hydroxyapatite in SBF and we named them as apatite nuclei [6].

In the previous study, we formed many micro pores on Ti plate by sulfuric acid (H_2SO_4) treatment, soaked the Ti plate in SBF, then precipitated apatite nuclei in the pores of the Ti plate by raising the temperature of the SBF [4, 5], and showed that thus treated Ti plate had a high bioactivity and a high adhesive strength to the formed hydroxyapatite layer. In the present study, we soaked Ti plate, with many micro pores on the surface formed by H_2SO_4 treatment, in SBF and heated the Ti plate directly by using electromagnetic induction to precipitate apatite nuclei in the pores. Similar to the previous study [4], the bioactivity was investigated by soaking in SBF and adhesive strength of formed hydroxyapatite layer to the Ti plate was measured.

2 Materials and methods

A commercially obtained pure Ti plate (JIS TP340, Kobe Steel, Japan) with $15 \times 10 \times 2\,mm^3$ in size was abraded with #800 abrasive paper, washed with acetone and distilled water in an ultrasonic cleaner, then dried at room temperature. The Ti plate was soaked in 48% H_2SO_4 solution at 90.0 °C for 60 min [1]. The H_2SO_4-treated Ti plate was washed with distilled water in an ultrasonic cleaner and dried at room temperature. We prepared SBF by dissolving reagent-grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$ and Na_2SO_4 in ultrapure water with the composition as shown in Table 1 and subsequently controlled this SBF at pH 8.00 with hydrochloric acid (HCl) and tris(hydroxymethyl)aminomethane ($(CH_2OH)_3CNH_2$) at 36.5 °C. The H_2SO_4-treated Ti plate was soaked in the solution and pressed by cold isostatic press (CIP-SI, Kobe Steel, Japan) in 392 MPa for 60 min in order to make the solution go into deep in the pores. Then we heated the Ti plate directly by using electromagnetic induction at 3 kW for 30 min while soaking in the solution. By this treatment, apatite nuclei were precipitated in the micro pores of the H_2SO_4-treated Ti plate and Apatite Nuclei Precipitated Titanium was obtained. The Ti plate was washed with distilled water and dried at room temperature.

Bioactivity of the Apatite Nuclei Precipitated Titanium was evaluated by soaking in SBF at pH 7.40, 36.5 °C. The surface of the Apatite Nuclei Precipitated Titanium was analyzed by thin film X-ray diffraction (TF-XRD; Rint 2500, Rigaku, Japan), scanning electron microscopy (SEM; ESEM-2700, Nikon, Japan) and energy dispersive X-ray analysis (EDX; DX-4, EDAX, USA).

	Ion Concentrations/mmol·dm^{-3}							
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
Human blood plasma	142.0	5.0	2.5	1.5	103.0	27.0	1.0	0.5
SBF	142.0	5.0	2.5	1.5	147.8	4.2	1.0	0.5

Table 1: Ion concentrations of human blood plasma and simulated body fluid (SBF).

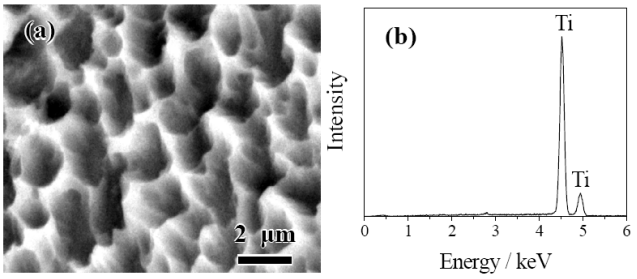

Figure 1: (a) SEM micrographs and (b) EDX profiles of the surface of the Ti plate after the soak in 48% H_2SO_4 solution at 90.0 °C for 60 min.

The adhesive strength of the formed hydroxyapatite layer to the Apatite Nuclei Precipitated Titanium plate was measured by a modified ASTM C-633 method [3]. Both sides of the Apatite Nuclei Precipitated Titanium were attached to stainless steel jigs ($10 \times 10\,mm^2$) by Araldite glue and tensile load was applied with universal testing machine (AGS-H Autograph, Shimadzu, Japan) at a cross head speed 1 mm·min^{-1} until fracture occurred.

3 Results and discussion

In Figure 1(a), SEM micrograph of the surface of the Ti plate after the H_2SO_4 treatment is shown. Micro pores around 1 μm orientated to various directions were observed. It is indicated that many micro pores were formed on Ti plate surface by H_2SO_4 treatment. In Figure 1(b), EDX profile of the surface of the H_2SO_4-treated Ti plate is shown. No peaks other than Ti were detected.

In Figure 2, SEM micrographs and EDX profiles of the surface of the Apatite Nuclei Precipitated Titanium plate after the soak in SBF at pH 7.40, 36.5 °C for various periods are shown. For 3 h sample, calcium phosphate film was not observed and peaks of phosphorous (P) and calcium (Ca), constituents of calcium phosphate, were not detected on the surface. For 6 h sample, it was observed that thin film covered the whole surface and peaks of P and Ca were detected. For 12 h sample, it was observed that needlelike crystals characteristic to hydroxyapatite covered the whole surface and peaks of P and Ca were detected.

In Figure 3, TF-XRD profiles of the surface of the Apatite Nuclei Precipitated Titanium plate after the soak in

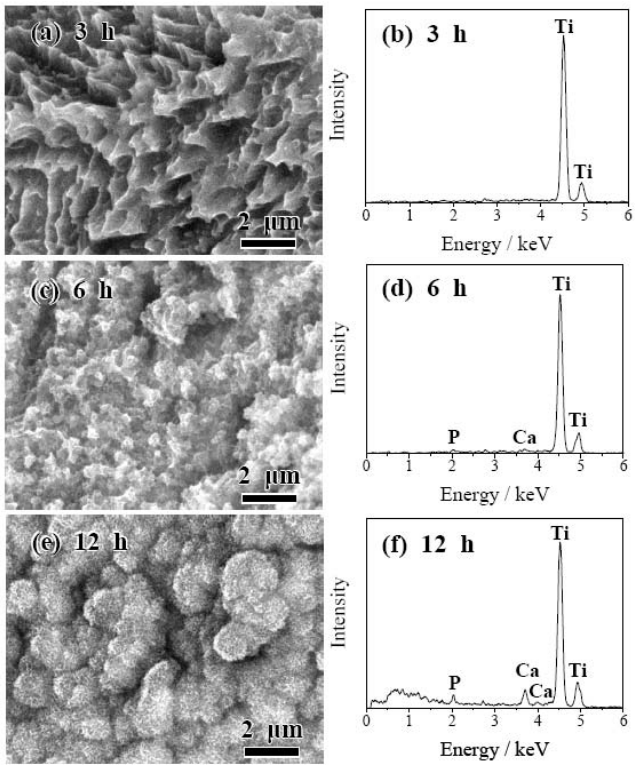

Figure 2: SEM micrographs and EDX profiles of the surface of the Apatite Nuclei Precipitated Titanium after the soak in SBF at pH 7.40, 36.5 °C (a) and (b) for 3 h, (c) and (d) for 6 h and (e) and (f) for 12 h.

SBF at pH 7.40 at 36.5 °C for various periods are shown. The profile before the soak is denoted as "0 h". For 0 h, 3 h and 6 h samples, no diffraction peaks of hydroxyapatite were detected. For 12 h sample, two diffraction peaks of hydroxyapatite were detected. For 24 h sample, four diffraction peaks of hydroxyapatite were detected. For 3 d, 7 d and 14 d samples, six diffraction peaks of hydroxyapatite were detected. The intensity and the number of diffraction peaks of hydroxyapatite increased with the soaking time. For the reference, the H_2SO_4-treated Ti plate was soaked in SBF at pH 7.40, 36.5 °C for 14 d. Hydroxyapatite formation was not detected for this plate.

By taking into consideration both the results of the SEM observation and the EDX analysis and TF-XRD profile, it is indicated that amorphous calcium phosphate covered the

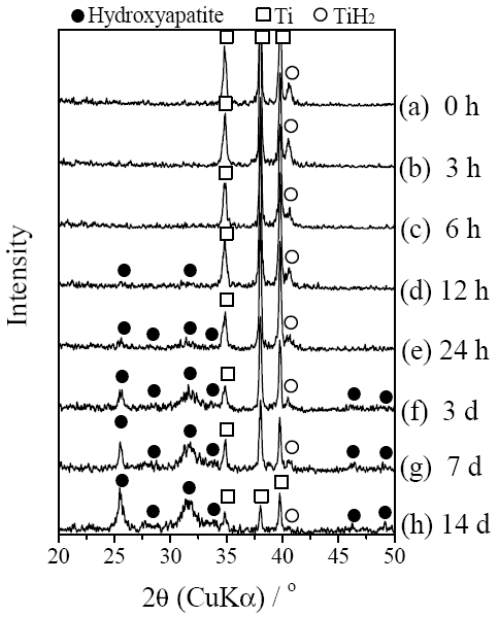

Figure 3: TF-XRD profiles of the Apatite Nuclei Precipitated Titanium plate after the soak in SBF at pH 7.40, 36.5 °C (a) for 0 h, (b) for 3 h, (c) for 6 h, (d) for 12 h, (e) for 24 h, (f) for 3 d, (g) for 7 d and (h) for 14 d.

whole surface of the Apatite Nuclei Precipitated Titanium after the soak in SBF for 6 h, then the amorphous calcium phosphate grew into hydroxyapatite within 12 h.

The adhesive strength between the formed hydroxyapatite and the Ti plate after the soak in SBF at pH 7.40, 36.5 °C for 14 d was 16.1 ± 3.0 MPa for 18 samples. High adhesive strength was obtained due to a mechanical interlocking effect between hydroxyapatite grown in the micro pores with various orientations and the Ti plate.

Previously, we precipitated apatite nuclei on H_2SO_4-treated Ti plate in SBF at pH 8.00, 36.5 °C by raising temperature of the fluid to 60.0 °C [4], where hydroxyapatite formation was detected after soaking in SBF at pH 7.40, 36.5 °C for 24 h, and the adhesive strength of hydroxyapatite layer was 8.4 ± 1.2 MPa. Both bioactivity and adhesive strength were further enhanced in the present study. Because the Ti plate was heated directly by using electromagnetic induction and then the precipitation condition of calcium phosphate was enhanced at the neighborhood of the Ti plate, it is considered that many apatite nuclei in fine particle size were effectively precipitated inside the micro pores. As a result, hydroxyapatite was induced in such short time and mechanical interlocking effect was effectively achieved.

4 Conclusions

Apatite nuclei were effectively precipitated in the micro pores of Ti plate treated by H_2SO_4 by direct heating of the Ti plate by using electromagnetic induction while soaking in SBF at pH 8.00 and Apatite Nuclei Precipitated Titanium was obtained. By soaking in SBF, amorphous calcium phosphate was induced and covered the whole surface of the Ti plate for 6 h, then grew into hydroxyapatite within 12 h. A high adhesive strength between the formed hydroxyapatite and the Ti plate was obtained. This material is promising for excellent implant materials with high mechanical property as well as high bioactivity.

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