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Evaluation of microstructure and some properties of hydroxyapatite/Ti composites

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The fabrication of a hydroxyapatite composite dispersed with Ti as a secondary phase was attempted. Hydroxyapatite/Ti composites were sintered either by pulse electric current sintering, PECS, or a hot-pressing method at various temperatures. The microstructure of hydroxyapatite/Ti composite was observed by scanning electron microscopy. Some mechanical properties and biological evaluation were performed. According to the biocompatibility results of these hydroxyapatite/Ti composites in an simulated body fluid (SBF) solution, hydroxyapatite-like crystals could be formed on the surface of these composites. The analysis of the microstructure of these composites and the relation between their microstructure and some properties were investigated.

Key words: Hydroxyapatite, Composites, Titanium, Microstructure, Biocompatibility.

Introduction

In biomedical and dental applications, the development of bioceramics is becoming increasingly important as the average age of humans increases. Among these bioceramics, hydroxyapatite is most attractive as the replacement inorganic material for bones and teeth because of its superior bioactive properties [1]. However, it possesses poor mechanical properties£¨such as low fracture toughness, fracture energy, and strength, in spite of its excellent biocompatibility [2].

On the other hand, Ti and its alloys show good biocompatibility, whereas in the case of other metals as biomaterials, the accumulation of toxic metal ions due to dissolution and corrosion in physiological environments in the body often leads to severe problems [3]. Further, the mechanical properties of Ti and its alloys are superior to those of bioceramics such as hydroxyapatite, other ceramics and glasses [4]. Therefore, in order to develop a high performance biomaterial for the replacement of bones and teeth, composites consisting of hydroxyapatite and Ti are thought to be one of the most promising groups of material.

For example, there have been many studies of hydroxyapatite coatings on Ti metal in order to add the bioactive properties to Ti. These were fabricated by dipping, sputtering, and plasma spraying methods etc. [5, 6]. For instance, the coating of hydroxyapatite on a Ti metal surface by a plasma spray method led to the decomposition of hydroxyapatite and resulted in tricalcium phosphates, calcium oxide etc. [7]. However, a detailed investigation of the reaction of Ti and hydroxy- apatite after a sintering process and the analysis of the interface structures between Ti and hydroxyapatite are limited and hardly well-understood. Therefore, a funda- mental evaluation of the microstructure of hydroxy- apatite/Ti composites prepared by a sintering process are significantly important in order to obtain the advan- tages of hydroxyapatite and Ti simultaneously. Also, there has never been a special study of hydroxyapatite/Ti composites fabricated by PECS technique.

Firstly, a description of an attempt at fabricating hydroxyapatite composites reinforced with Ti metal phase will be given in this paper. The main purpose is to fabricate hydroxyapatite/Ti composites by PECS or by a hot-pressing method. The second purpose is to evaluate the microstructure of hydroxyapatite/Ti composites and the relation between their microstructure and some mechanical properties. Finally, the biocompatibility of these composites was evaluated in a simulated body fluid (SBF) developed by Kokubo *et al*. [8-10]. The effect of the difference of sintering method on the microstructure and properties will also be dis- cussed.

Experimental Procedure

The starting powder was hydroxyapatite with a primary particle size of 0.2 μm, which was commercially available from Taihei Chemical, Co., Ltd. (Japan). Hydroxyapatite powder granulated by splay drying method has a mean diameter size of 20 μm was. The content of impurities are shown in Table 1. Ti powder was provided by Osaka Titanium Co. Ltd. (Japan) and

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Table 1. Characteristics of hydroxyapatite powder

Particle size	Specific surface area			Primary particle size		
18 μm	37 m^2/g			0.2 μm		
Impurities	SO_4	Cl	Fe	Mg	Mn	Pb
	<0.3%	<0.1%	0.02%	0.5%	0.01%	<20 ppm

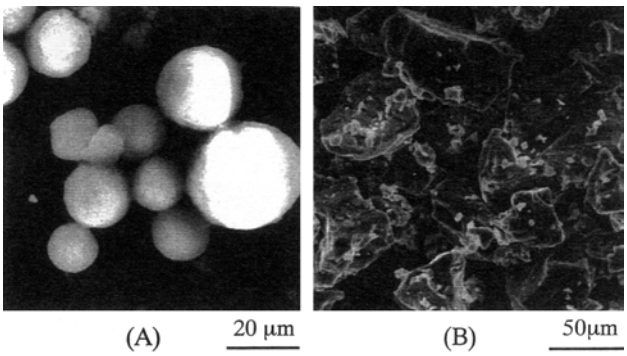

Fig. 1. SEM images of hydroxyapatite powder (A) and Ti powder (B).

had an average particle size of 50 μm. The microstructures of both starting powders are shown in Fig. 1. Hydroxyapatite/Ti powders (80/20 vol% and 75/25 vol%) were mixed using a wet-ball milling method. The mixing was done in ethanol for 12 h using ZrO_2 milling media in the plastic pot. After the wet-ball milling process, the mixed slurry of hydroxyapatite/Ti was dried at 50-60°C in an evaporator. Approximately 20 g of the mixed powder was hot-pressed at 800 to 1000°C with a heating rate of 25°C/minute in an Ar atmosphere. The applied pressure for hot-pressing was 30 MPa. After holding at the hot-pressing temperatures for 1h, the samples were cooled in the furnace to room temperature.

Alternatively, the mixture of hydroxyapatite and Ti was sintered by a PECS technique (Dr Sinter: Sumitomo Coal Mining). About 15 g of the powders was sintered in a graphite mold by this PECS method. The composite powders were heated at 100°C/minute and held for 5 minute at the sintering temperature in an Ar atmosphere. PECS sintering was performed at 800 to 1000°C under an applied pressure of 30 MPa.

The hot-pressed or PECSed hydroxyapatite/Ti samples were diamond ground and test specimens were cut from the bulk ground samples. The dimensions of cut samples were $3 \times 4 \times 35$ mm. The surfaces of the specimens were polished with diamond paste to a mirror-like finish. The identification of the phase in these samples were made with a Rigaku-RINT2500 diffractometer (XRD) using Ni-filtered Cu-Kα radiation. The bulk densities of the sintered samples were determined by Archimedes' method after the samples had been boiled in water for 1h. Etching was done in an acetic acid solution. Microstructural observations of polished and etched surfaces were performed with a scanning electron microscope (SEM: S-800, Hitachi). Specimens of composites for investigation of fracture characteristics were rectangular with dimensions of $2 \times 3 \times 25$ mm. These samples were notched with a diamond wheel of 0.2 mm thickness. A straight-through notch with a relative length, $a_0/w = 0.5$, was sharpened to a radius < 10 μm. A cross-head speed of 0.1 mm/minute with a span of 20 mm in a three-point bending test was used. The fracture energy of these composites was measured with a single edge double-notched beam (SEDNB) method [11]. Load displacement curves were recorded during stable crack propagation. The fractured surfaces of the composites after the fracture tests were observed with a SEM.

The *in-vitro* biological evaluation of these hydroxyapatite/Ti composites was performed in a simulated body fluid (SBF), which was developed by Kokubo *et al.* [8-10]. After the immersion in a SBF solution at 36.5°C in the incubator for 7-14 days, samples of these composites were observed by SEM.

Results and Discussion

Figure 2 show XRD results for hydroxyapatite/20 vol% Ti composites hot-pressed at 800-1000°C. The hydroxyapatite/Ti composite hot-pressed at 800°C was composed of mainly hydroxyapatite, Ti_3O, and Ti_2O with a minor unknown phase. Hot-pressing at 900°C gave composites which were composed of hydroxyapatite, Ti_3O and in part Ti_2O. The samples prepared by hot-pressing at 1000°C consisted of hydroxyapatite,

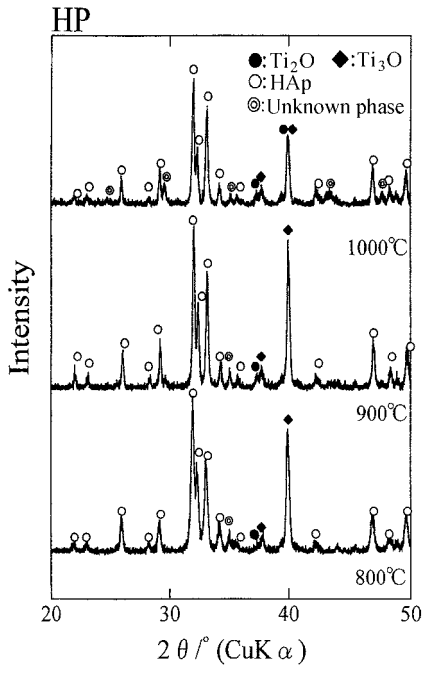

Fig. 2. XRD patterns of hydroxyapatite/20 vol% Ti composites hot-pressed at 800-1000°C.

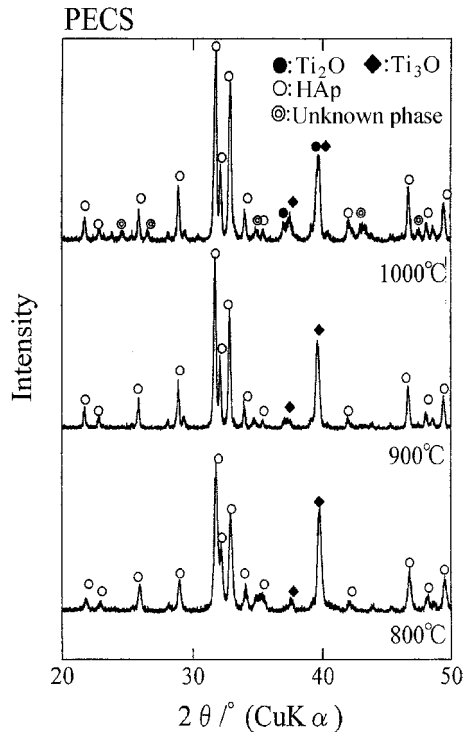

Fig. 3. XRD patterns of hydroxyapatite/20 vol% Ti composites prepared by a PECS process at 800-1000°C.

Ti_3O, Ti_2O, and an unknown phase. The amount of this unknown phase increased with the hot-pressing temperatures for hydroxyapatite/20% Ti composites. By contrast, XRD patterns of these composites prepared by the PECS technique are shown in Fig. 3. The compo- sites fabricated by PECS at 800 and 900°C had hydroxyapatite and Ti_3O phases without other unknown phases, whereas Ti_2O phases and another unknown phase were confirmed for composites prepared by hot-pressing at 800°C. Furthermore, hydroxyapatite, Ti_3O, Ti_2O, and an unknown phase were identified for hydroxyapatite/Ti composites prepared by PECS at 1000°C. From the comparison of XRD patterns for hydroxyapatite/Ti composites sintered by hot-pressing and the PECS method, the formation of both Ti_2O and the unknown phase was found to be inhibited in the case of PECS technique.

The polished surfaces of samples were etched in 0.1 N acetic acid solution. The microstructures of samples observed by SEM are shown in Fig. 4. The matrix of hydroxyapatite for all samples prepared at 800-1000°C was composed of fine equiaxed grains. The grain size increased with the hot-pressing temperature. For samples hot-pressed at 1000°C, the grain size of the hydroxyapatite matrix was approximately

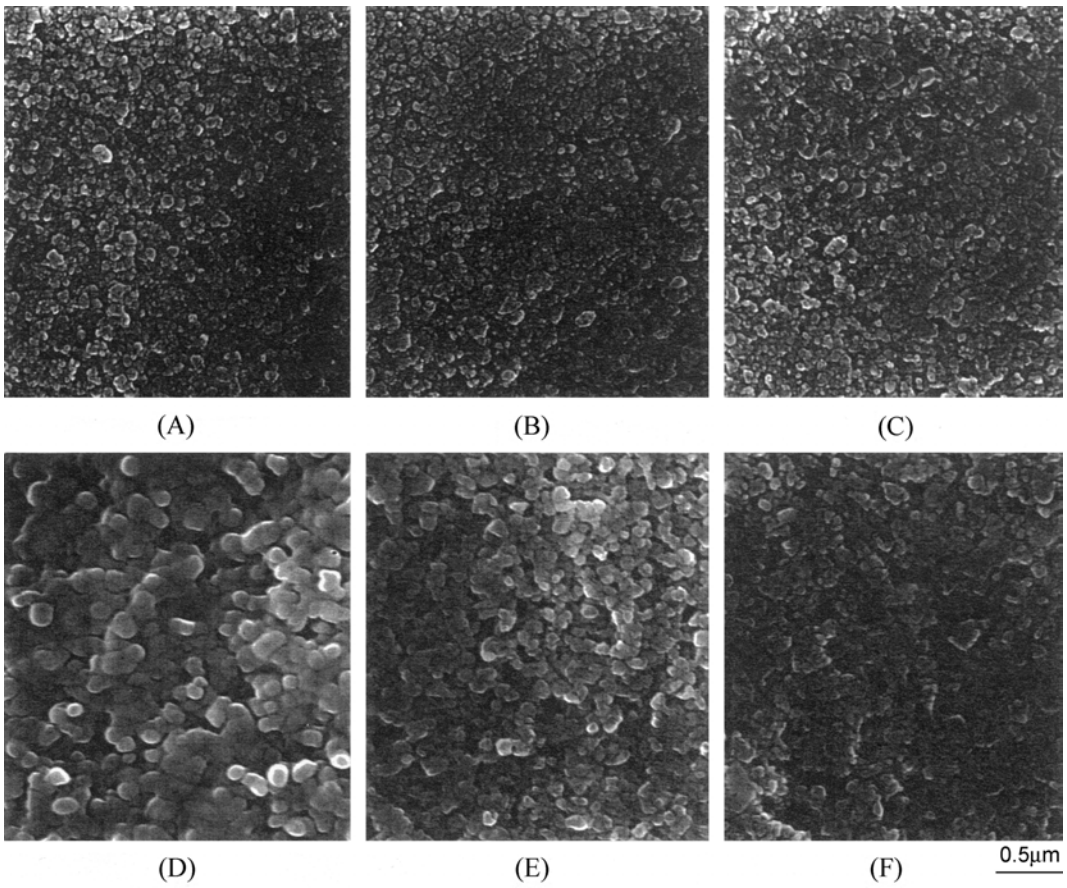

Fig. 4. SEM images of hydroxyapatite/Ti composites prepared by hot-pressing and PECS at 800-1000°C. (A) hot-pressed at 800°C (B) hot-pressed at 900°C (C) hot-pressed at 1000°C. (D) PECS at 800°C (E) PECS at 900°C (F) PECS at 1000°C. Bar shows 500 nm.

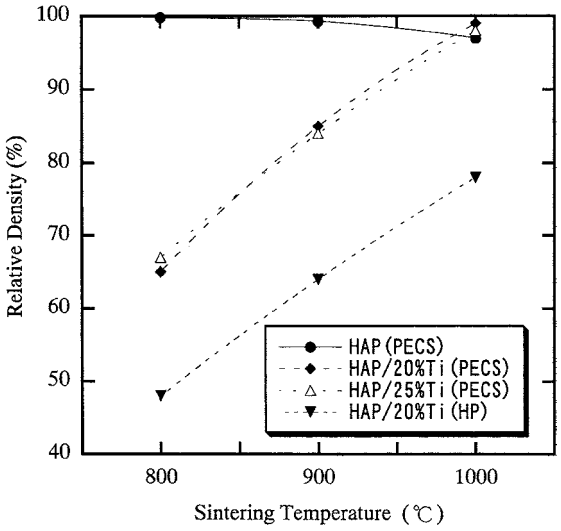

Fig. 5. Variations of the density with sintering temperature for hydroxyapatite/Ti composites prepared by hot-pressing (HP) and PECS techniques.

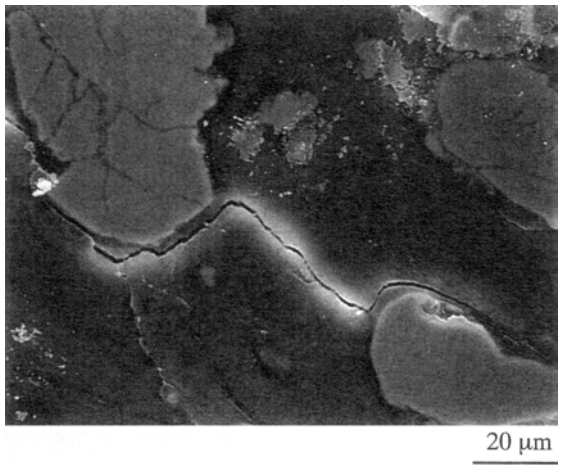

Fig. 6. SEM image of crack propagation in a hydroxyapatite/20 vol% Ti composite prepared by the PECS technique at 900°C.

200 nm. Ti grains as a secondary phase were observed to be dispersed in the matrix with the same angular shape as in the starting powder, are not shown here. However, the matrix of hydroxyapatite/Ti composites prepared by PECS was finer than those of samples prepared by hot-pressing, as is evident in Fig. 4. Even at 1000°C, the matrix of the composites was composed of nanometre-sized hydroxyapatite grains with an average grain size below 100 nm. It became obvious that fabrication by PECS could lead to a finer-structured matrix for dense hydroxyapatite/Ti composites than by the hot-pressing technique.

The variations of the density with sintering temperature for hydroxyapatite/Ti composites prepared by hot-pressing and the PECS techniques are shown in Fig. 5. In the case of the composites prepared by PECS, the density of composites tended slightly to decrease with the sintering temperature. The density of these composites was approximately 65% at 800°C and 85% at 900°C, respectively. Fully dense hydroxyapatite/Ti composites were obtained at 1000°C by the PECS method in this study. Monolithic hydroxyapatite was fully densified at 700-800°C by the PECS technique.

By contrast, hydroxyapatite/20 vol% Ti composites prepared by the hot-pressing technique exhibited relatively lower densities, compared to the composites sintered using the PECS method. Hot-pressing at 800°C gave samples which were densified to approximately 50% of theoretical density. Although the density of samples increased with the hot-pressing temperature. hydroxyapatite/Ti composites hot-pressed at 1000°C showed at most approximately 80% of theoretical density. Monolithic hydroxyapatite was densified at 1100-1200°C by the hot-pressing method [12]. Therefore, it was found that with the addition of Ti into the hydroxyapatite matrix, the densification of hydroxyapatite for the composites fabricated by the hot-pressing technique was significantly inhibited, in comparison with the results of those composites sintered using the PECS method.

The fracture energies of monolithic hydroxyapatite and hydroxyapatite/Ti composites prepared by the PECS technique at 900°C were measured. Monolithic hydroxyapatite showed a low fracture energy of 1.0 J/m^2, which value is almost in agreement with those reported by other researchers [13]. However, the fracture energy of hydroxyapatite/Ti composites prepared by the PECS technique at 900°C increased with the Ti content. These fracture energies were 9 J/m^2 for hydroxyapatite/20 vol% Ti and 20 J/m^2 for hydroxyapatite/25 vol% Ti composites. Figure 6 shows an SEM image of crack propagation in a hydroxyapatite/20 vol% Ti composite prepared by the PECS technique at 900°C. The crack was observed to be deflected and bridged around a Ti grain. Champion *et al.* reported their results on the mechancal properties of hydroxyapatite reinforced with Al_2O_3 platelets [14]. According to their report, the fracture toughness of hydroxyapatite was improved by crack deflection, crack branching, bridging and crack debonding by the platelets. Therefore, the energy dissipative mechanism of reinforcements present as a secondary phase could play an important role in the reinforcement of hydroxyapatite-based composites. In this study, the increase of fracture energy of hydroxyapatite/Ti composites prepared by the PECS technique is thought to be attributed to the deflection and bridging by the addition of Ti as a secondary phase.

Figure 7 shows *in-vitro* results after the immersion in 1.0 SBF solution at 36.5°C for 14 days. SEM images show the hydroxyapatite-like precipitation on the surface of monolithic hydroxyapatite, and hydroxyapatite/20 vol% Ti composites prepared by the PECS technique at 900°C, and hydroxyapatite/20 vol% Ti composites sintered by the hot-pressing technique at 900°C.

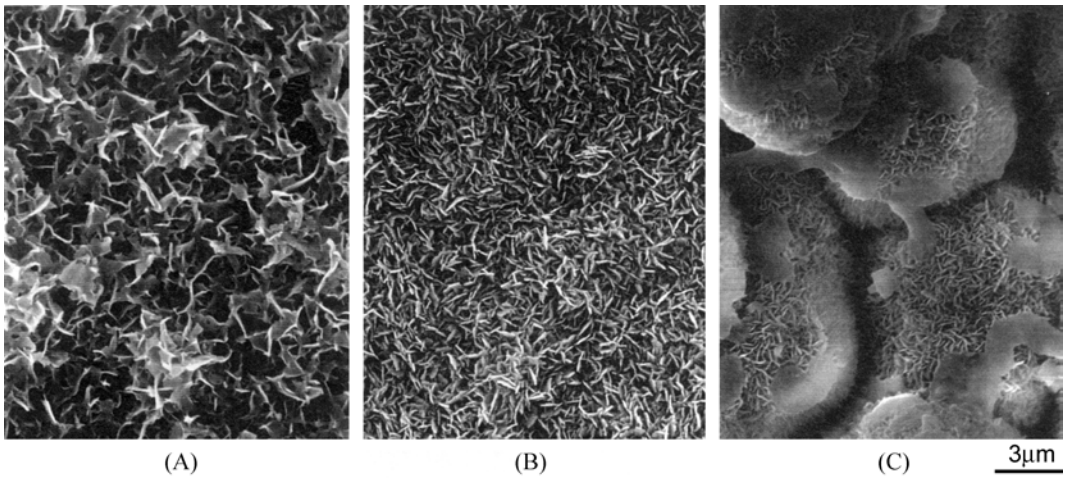

Fig. 7. SEM images of the precipitation on the surface of monolithic hydroxyapatite (A), hydroxyapatite/20 vol% Ti composite prepared by the PECS technique at 900°C (B) and hydroxyapatite/20 vol% Ti composite prepared by the hot-pressing technique at 900°C (C) after immersion in SBF solution at 36.5°C for 14 days.

Although all of the samples showed biocompatibility, the hydroxyapatite/Ti composites prepared by the PECS technique possessed biocompatibility as good as monolithic hydroxyapatite, as is clearly shown in Fig. 7. However, the bioactivity of hydroxyapatite/Ti composites prepared by the hot-pressing technique was lower than those of monolithic hydroxyapatite and the composites prepared by PECS. This relatively low bioactivity for hydroxyapatite/Ti composites prepared by hot-pressing is thought to be due to the decrease of hydroxyapatite phase caused by the formation of Ti_3O and Ti_2O, and the unknown phase. Accordingly, these results on the evaluation of *in-vitro* bioactivity suggest that hydroxyapatite/Ti composites prepared by the PECS method had good bioactivity similar to that of monolithic hydroxyapatite.

Conclusion

Hydroxyapatite/Ti composites were fabricated by sintering a mixture of hydroxyapatite and 20-25 vol% Ti powders through either a hot-pressing or PECS technique. Microstructures and some properties of these hydroxyapatite composites dispersed with Ti were investigated.

In the case of the hot-pressing technique, the densities of these hydroxyapatite/Ti composites gave a range of 50-80% of theoretical density and fine-microstructures with the average matrix grain size of 200-300 nm, in the case of a sample hot-pressed at 1000°C as observed by SEM. These composites with a Young's modulus matching that of cortical bones were prepared by a hot-pressing method in the present study. On the other hand, those composites prepared by the PECS method gave dense composites which tended to increase in density with the sintering temperature. Fully dense hydroxyapatite/Ti composites were successfully obtained at 1000°C by the PECS method. Hydroxyapatite/25 vol% Ti composites prepared by the PECS technique at 900°C possessed high fracture energy, caused by the deflection and bridging by the addition of Ti as a secondary phase, compared with monolithic hydroxyapatite. Also, hydroxyapatite/Ti composites prepared by the PECS technique possessed good biocompatibility, similar to that of monolithic hydroxyapatite.

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