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Surface bio-modification of titanium implants by an enamel process

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A bioactive bio-enamel was prepared by coating two different glasses on a titanium metal in sequence, the first coat was for better bonding between a bio-enamel and the titanium and the second coat for promoting its bioactivity, which means hydroxyapatite formation. The ground glass coat and bioactive glass coat were fired at 900 °C for 5minutes and 850 °C for 30 seconds in an Ar atmosphere, respectively. The hydroxyapatite forming behavior on the bio-enamel was compared with that on the bulk bioactive glass with the same composition of the bio-enamel. The rate of hydroxyapatite formation on the bio-enamel was much faster than that on the corresponding bulk bioactive glass. The behavior of hydroxyapatite formation also improved when the bulk bioactive glass was heat-treated at 850 °C for 20 seconds. It is believed that the heat-treatment of the glasses makes the leaching of cations from the glass surface easier and enhances the rate of the hydroxyapatite formation.

Key words: bioactive glass, titanium, bio-enamel. hydroxyapatite, silica-rich layer.

Introduction

Titanium has been used as orthopedic implant materials because of its high mechanical strength and bio-compatibility [1]. The bonding behavior of titanium-based prostheses to a living tissue, however, is not satisfactory like some other bioactive materials, such as hydroxyapatite and bioactive glasses, which directly bond to a human bone.

In order to provide bioactivity to titanium, therefore, titanium metal is often coated with synthetic hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$], which is very similar to the inorganic components of a bone and has proven to be bioactive. The most commonly used technique to fabricate hydroxyapatite-coated titanium is a thermal plasma spray [2]. However, the chemical composition and structure of the hydroxyapatite coat are often changed during the plasma processing due to its high temperature, and this affects its bioactivity. One of the other problems of this bio-material is the poor bonding state between the titanium and hydroxyapatite, and this poor adhesion between two materials causes the fracture between this implant and bone [3-4].

Bioactive glass is one of the most biologically-active biomaterials that can bond chemically to a living tissue [5]. The major drawback of this glass, however, is its low mechanical strength. A silica-rich layer is also developed on the surface of bioactive glass when implanted, and this silica gel layer acts as a fracture origin. Therefore, it is hard to use this glass alone in a load-bearing position in a body [6].

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One of the methods to increase its mechanical strength is to coat this glass on stronger materials, such as alumina ceramics or metals. When the glass is coated on a titanium metal substrate, which is chosen for this study, the air spray technique is often used because of its convenience in the control of the thickness of the glass coat and fabrication [7, 8]. The coefficient of thermal expansion of a bioactive glass is usually much higher than that of a titanium substrate, and this mismatch of the thermal expansions may cause cracks in the glass layer. In this study, therefore, another glass was coated between the bioactive glass and titanium metal in order to buffer their thermal expansion differences. This technique is often applied in an enamel process.

Therefore, the primary objectives of this work are to apply bioactive glass on a titanium substrate without cracks, and to examine the hydroxyapatite-forming behavior on the bioactive glass coat layer depending on the heat-treatment. The hydroxyapatite-forming behavior of the bio-enamel is also compared to that of the bulk bioactive glass with the same composition as that of the bio-enamel.

Experimental Procedure

Preparation of bioglass-coated titanium

Two different glasses were prepared as shown in Table 1. One was for a ground-coat glass and the other was for a bioactive cover glass, which is now called a bio-enamel. Appropriate amounts of raw materials, from the reagent grades of SiO_2, $CaCO_3$, Na_2CO_3, H_3PO_4, B_2O_3 and Al_2O_3, were weighed and mixed in a gyro-blender for 2 hours. Then, each glass batch was melted in a Pt-Rh crucible in an electrically heated furnace at a

Table 1. The composition of the glass coats (mole%)

Name \ Ccomposition	SiO_2	Na_2O	CaO	B_2O_3	Al_2O_3	P_2O_5
Ground coat	55	10	25	5	5	–
Bio-enamel	50.1	9.2	32.3	5	–	3.4

temperature of 1450 °C. The glass melt was quenched on a stainless steel plate and was pulverized into powder with a size of less than 10 mm in a planetary agate mill. The coefficients of thermal expansion for these glass samples were 93×10^{-7}/°C for the ground-coat glass and 108×10^{-7}/°C for the bio-enamel, respectively The coefficient of thermal expansion of pure titanium used in this study was 88×10^{-7}/°C.

The glass powder was suspended in an acetone solution and was spray-coated on to a pure titanium substrate. The medical grade of titanium (ASTM grade 2) was cut to the size of 15×15×1 mm and polished with SiC sandpaper (#2000) and kept in acetone. The sprayed samples were fired in a tube furnace at various temperatures. An argon atmosphere was used in the furnace. The ground coat was fired at 900 °C for various times and the bioactive glass coat. which is the bio-enamel, was fired at 850 °C for various times. The thickness of the coat was 10 μm for the ground coat and 20 μm for the bio-enamel layer.

For the bulk glass experiment, the glass melt was cast in a graphite mold to make a bar, and then the glass bar was annealed at 550 °C before cutting.

Preparation of simulated body fluid and reaction of the bioglass-coated titanium

To examine the hydroxyapatite formation on the bioglass-coated titanium, the fabricated sample was reacted in simulated body fluids (SBF). The SBF was prepared by dissolving NaCl, KCl, $NaHCO_3$, $K_2HPO_4\cdot 3H_2O$, $MgCl_2\cdot 6H_2O$, $CaCl_2$ and Na_2SO_4 in tris(hydroxymethyl)-aminomethane[$(CH_2OH)_3CNH_2$] with a pH 7.3, as described by Kokubo et al. [9]. The ion concentrations in the solution are almost the same as those of human blood plasma. The prepared samples were suspended in a sealed polyethylene bottle that contained 22.7 ml of SBF. The surface area of the sample to the volume of the solution ratio was 0.1 cm^{-1} and the reaction was carried out at 37°C for various times.

Analysis of the reacted surface

The reacted surface of the bio-enamel was analyzed with a thin film X-ray diffractometer (Philips PW3719 operated at 40 kV, 1.5° as an incident beam angle, Cu target, scan speed: 0.08/s, 2θ: 10-60°). The hydroxyapatite crystalline morphology was also examined with a scanning electron microscope (Hitachi X-4200, 20 kV) and ion contents of the reacted surface was examined with an Energy Dispersive X-Ray Microanalyzer (EDX) attached at the scanning electron microscope.

Fourier Transform-Infrared Spectrometer (Bio-Rad, FT-165) attached to a diffused reflection unit was also applied to examine the glass surfaces as well as the reacted sample surfaces. The IR spectra were obtained in the range of 400-1200 cm^{-1} with a resolution of 2 cm^{-1}.

Measurement of ion concentration in reacted SBF

The concentrations of Si^{4+} and P^{5+} ions in the reacted SBF were measured by a molybdenum blue method. By adding ammonium paramolybdate solution, the Si^{4+} and P^{5+} ions in the solution turned into silicomolybdate and phosphomolybdate, respectively [10]. The extinctions at 810 nm caused by silicomolybdate and 885nm caused by phosphomolybdate were measured by a UV-visible spectrometer (Shimadzu, UV-2401PC). All extinctions were compared to a standard calibration curve to calculate these ion concentrations.

The concentration of Ca^{2+} ions was examined by an atomic absorption spectrophotometer (Thermo Jarrell Ash Corporation, AA-Scan1).

Results and Discussion

Hydroxyapatite formation on the bioactive glass-coated titanium

The ground coat glass was fired at 900 °C for various times in an Ar atmosphere and their thin film X-ray diffractometer (XRD) results are shown in Fig. 1.

When the ground coat was fired for less than 5

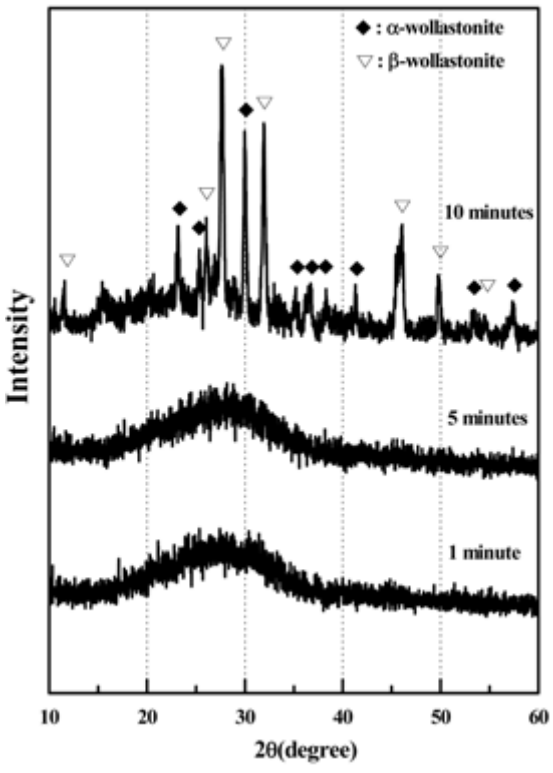

Fig. 1. Thin Film XRD patterns of the ground coat glass. The ground coat was heat-treated at 900 °C for various times.

minutes, the ground coat layer remained as an amorphous phase and a smooth surface was obtained. When the ground coat was fired for 10 minutes, however, the glass layer crystallized into α- and β-Wollastonite. The ground coat fired for 5 minutes was chosen because of its good adhesion to the titanium metal. This short firing schedule also minimizes the Ti- ion diffusion from the Ti-metal to the ground coat glass [11]. Ti ions in a bioactive glass are known as a component that suppresses the ability of hydroxyapatite formation in a bioactive glass [12].

Bio-enamel, the cover coat, was fired at 850 °C for 3 and 15 minutes and then reacted in SBF for 12 hours. The relevant XRD results are presented in Fig. 2.

When the bio-enamel coat was fired for 3 minutes, no crystalline phase was observed, and a somewhat broadened peak of apatite showed up after the reaction in SBF. This indicates that new crystals were formed after the reaction in SBF. The broad peak at 2θ=32° ~35° in Fig. 2(a) means that the hydroxyapatite developed on this sample had a highly disordered structure.

When the bio-enamel was fired for 15 minutes, however, the coat layer crystallized into apatite and $Na_2Ca_3Si_6O_{16}$ crystals. After the reaction of this sample in SBF for 12 hours, peaks from $Na_2Ca_3Si_6O_{16}$ crystals disappeared but peaks from apatite remained. The peak intensities of this apatite shown here were stronger when compared with the data of Fig. 2(a) and each peak was clearly separated. This indicates that the apatite peaks in this diffraction pattern is not from the precipitated hydroxyapatite in the SBF, but the apatite which crystallized during the heat-treatment. It is believed that calcium and phosphorus ions, which are essential for the formation of hydroxyapatite, are used up when the bio-enamel coat crystallized into apatite and $Na_2Ca_3Si_6O_{16}$ crystals. An absence of releasing calcium and phosphorus ions from this sample hinders the formation of hydroxyapatite.

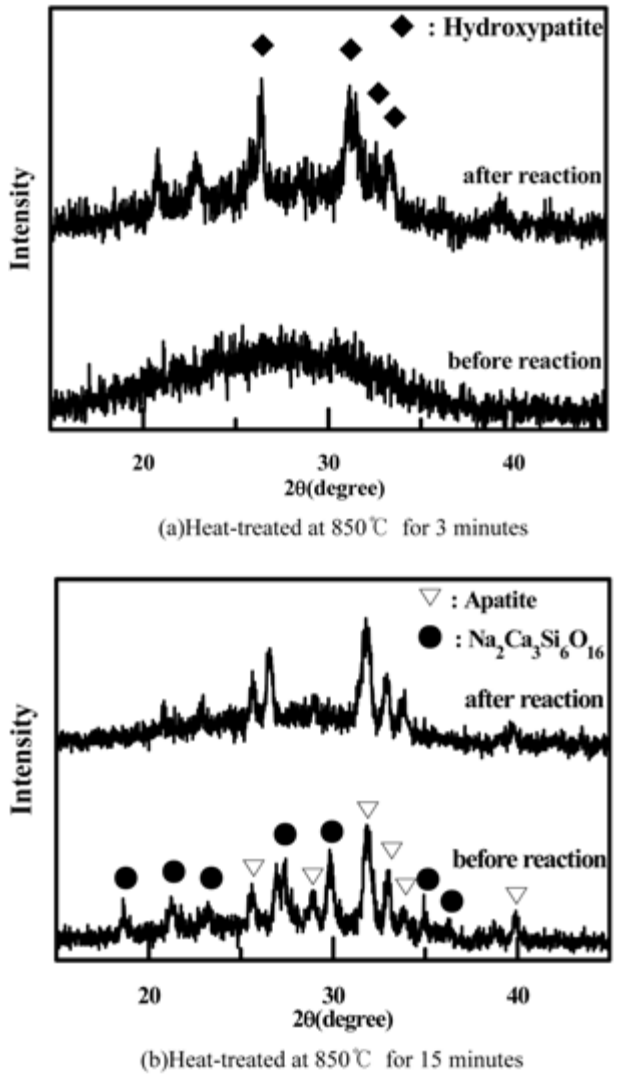

Fig. 2. Thin Film XRD patterns of the bio-enamel before and after the reaction in simulated body fluid for 12 hours.

Formation of hydroxyapatite on bulk bioactive glass and heat-treated bulk glass

Bulk bioactive glass, which has the same composition as the bio-enamel, was reacted in SBF for various times to evaluate the bioactivity and their FT-IR results are shown in Fig. 3.

After 72 hours of reaction, the peak of non-bridging

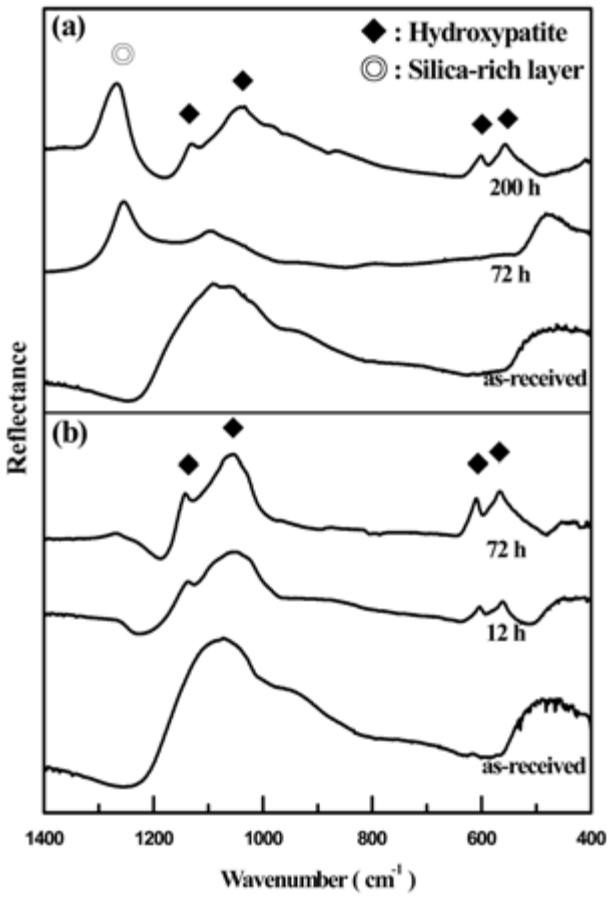

Fig. 3. FT-IR spectra of (a) a bulk glass and (b) bio-enamel after the reaction in simulated body fluid for various times.

oxygen at 930 cm^{-1} disappeared due to the leaching of modifying cations and the peak of a silica-rich layer at 1240 cm^{-1} appeared. In a bioactive glass, it is widely believed that the hydroxyapatite is formed on the silica-rich layer made by leaching of various ions, such as Na and Ca [13]. As the reaction time increased up to 200 hours, peaks of the P-O bending vibration peaks were observed at 600 and 560 cm^{-1}, which is a good indication of hydroxyapatite formation on the glass surface [14]. For the bio-enamel, on the other hand, hydroxyapatite peaks showed up within 12 hours of reaction in the SBF. These peaks sharpened as the reaction time passed. This result indicates the ability of hydroxyapatite formation promoted by an enameling process. In this case, no peak of a silica-rich phase was observed.

To examine the effect of heat-treatment on the hydroxyapatite formation, a bulk glass bar was cut into rectangular specimens 15×15×1 mm and fired from 10 to 60 seconds. Heat-treated samples were reacted in SBF for 12 hours, and their FT-IR results are shown in Fig. 4.

No significant glass structural change was observed after the heat-treatment using FT-IR. After reaction for 12 hours in SBF for the sample without heat-treatment (Fig. 4-b), the peaks of Si-O-Si stretching at 1068 cm^{-1} shifted to 1095 cm^{-1} and the peak of non-bridging oxygen (Si-O) at 930 cm^{-1} moved to 924 cm^{-1} because of the leaching of cations. In the samples fired for 10 seconds (Fig. 4-c), however, the peak of non-bridging oxygen disappeared and a silica-rich layer showed up. This result means that the rate of ion leaching from the glass was accelerated by heat-treatment.

When the bulk glass was heat-treated for 1 minute, the sample partially crystallized. No silica rich layer was observed on this sample when it was reacted in SBF for 12 hours, but only small peaks of crystallized apatite was detected..

Among these samples, glass with a heat-treatment for 20 seconds was chosen and reacted in SBF for various times. The FT-IR spectra are presented in Fig. 5.

The peak from a silica-rich layer showed up after 12 hours of reaction, and a "bump" around 550~600 cm^{-1} was observed after 48 hours of reaction. This bump seems to indicate an amorphous Ca-P film. Kim et al. [13, 15] argued that an amorphous calcium phosphate film formed on the SiO_2-rich layer first and that the amorphous film transformed to a hydroxyapatite crystalline phase by combining with OH^- and CO_3^{2-} from the solution. Well-developed hydroxyapatite peaks were observed after 72 hours of reaction. As shown in Fig. 3(a), however, no hydroxyapatite was formed until 200 hours of reaction in the bulk bioactive glass without heat-treatment. This result indicates that the heat-treatment of bioactive glass promotes the leaching of cations as well as an ability for hydroxyapatite formation.

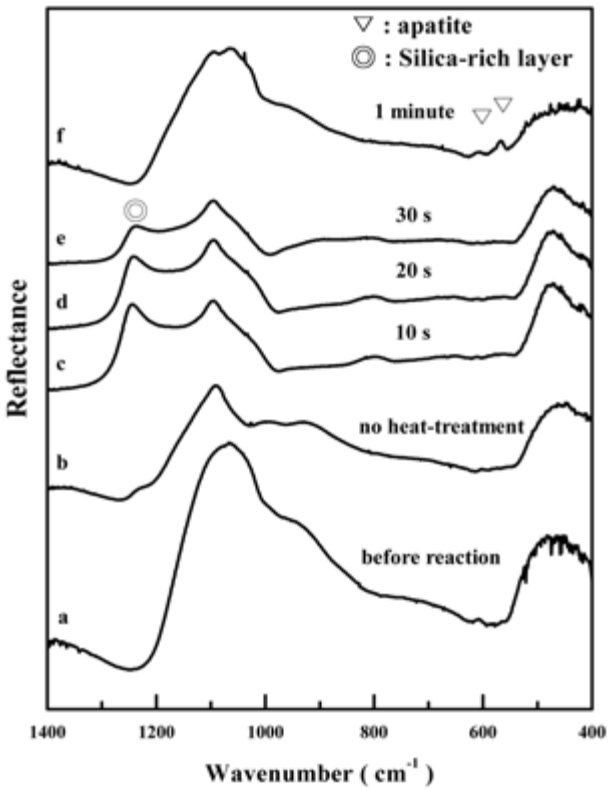

Fig. 4. FT-IR spectra of bulk bioactive glass, which was heat-treated at 850 °C for various times, after the reaction in simulated body fluid for 12 hours.

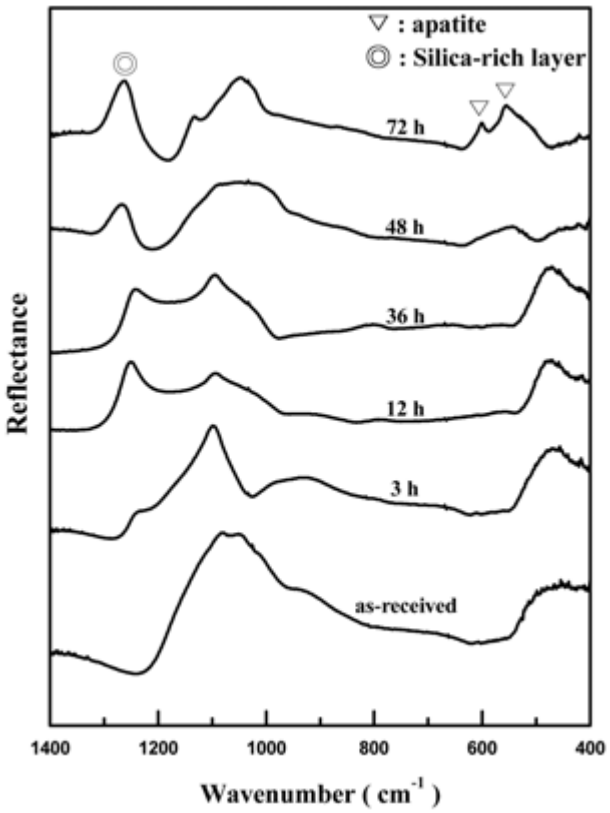

Fig. 5. FT-IR spectra of the bulk bioactive glass, which was fired at 850 °C for 20 seconds, after the reaction in simulated body fluid for 12 hours.

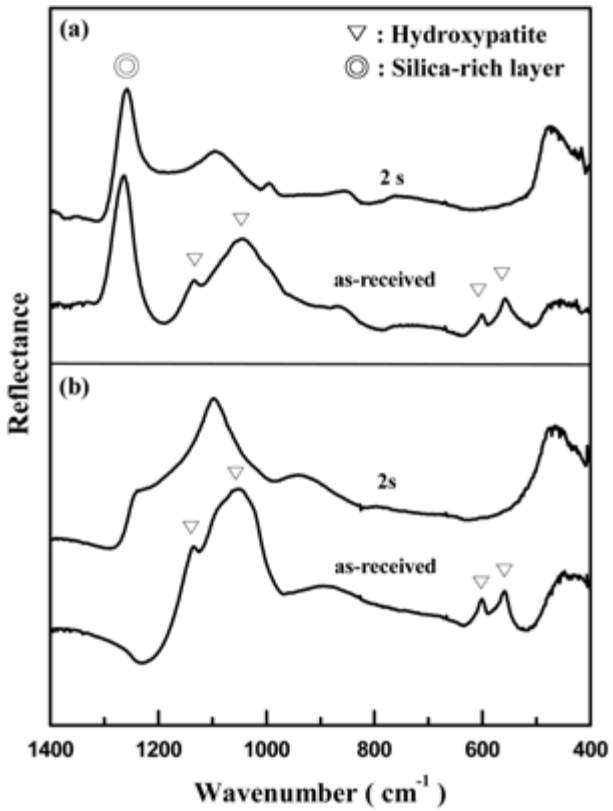

Fig. 6. FT-IR spectra of (a) bulk bioactive glass and (b) bio-enamel after immersion in HCl solution with a pH 1 to remove hydroxyapatite.

Formation of a silica-rich layer on the bioactive glass and bio-enamel

When bioactive glass was reacted in SBF, it has been believed that hydroxyapatite precipitated onto the silica-rich layer that was developed by the leaching of cations from the glass [9]. This fragile silica-rich layer is a major drawback of bioactive glass for use as an implant in a human body. To examine the presence of the silica-rich layer underneath the newly formed hydroxyapatite, two different samples were prepared as follows. First, a bio-enamel was reacted in SBF for 12 hours to obtain hydroxyapatite, and this was followed by dissolving the hydroxyapatite by treating the sample in HCl with a pH of 1 for 2 seconds. Second, the bulk bioactive glass, which has the same composition as the bio-enamel, was reacted in SBF for 200 hours to obtain hydroxyapatite on the glass surface and immersed in HCl solution for 2 seconds.

Figure 6 shows the FT-IR spectra of these samples after dissolving out the hydroxyapatite in HCl solution. In the case of the bulk bioactive glass, the peaks of hydroxyapatite disappeared after 2 seconds of immersion and the typical spectra from the silica gel at 1260 cm^{-1} still remained. However, in the spectra of the bio-enamel, no typical spectra of silica gel were observed after immersion in HCl. The morphology of SEM and EDX analysis for the surfaces of both HCl-treated samples are shown in Fig. 7.

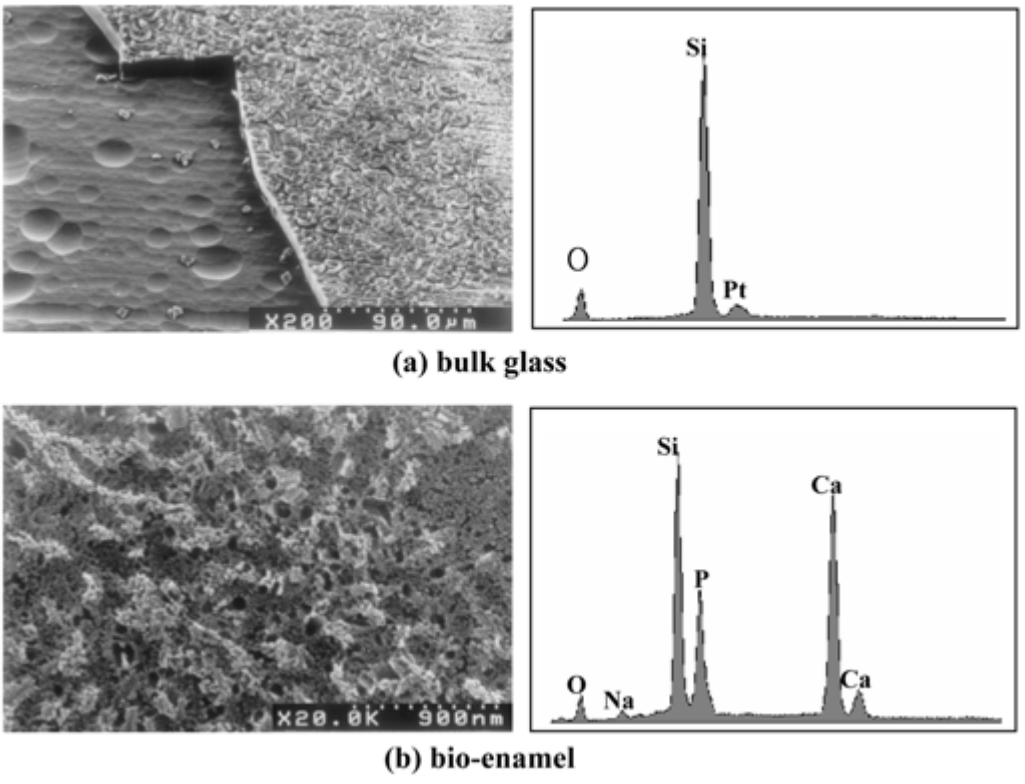

Fig. 7. SEM micrographs and EDX analyses of (a) bulk bioactive glass and (b) bio-enamel after immersion in HCl solution with a pH 1 to remove hydroxyapatite.

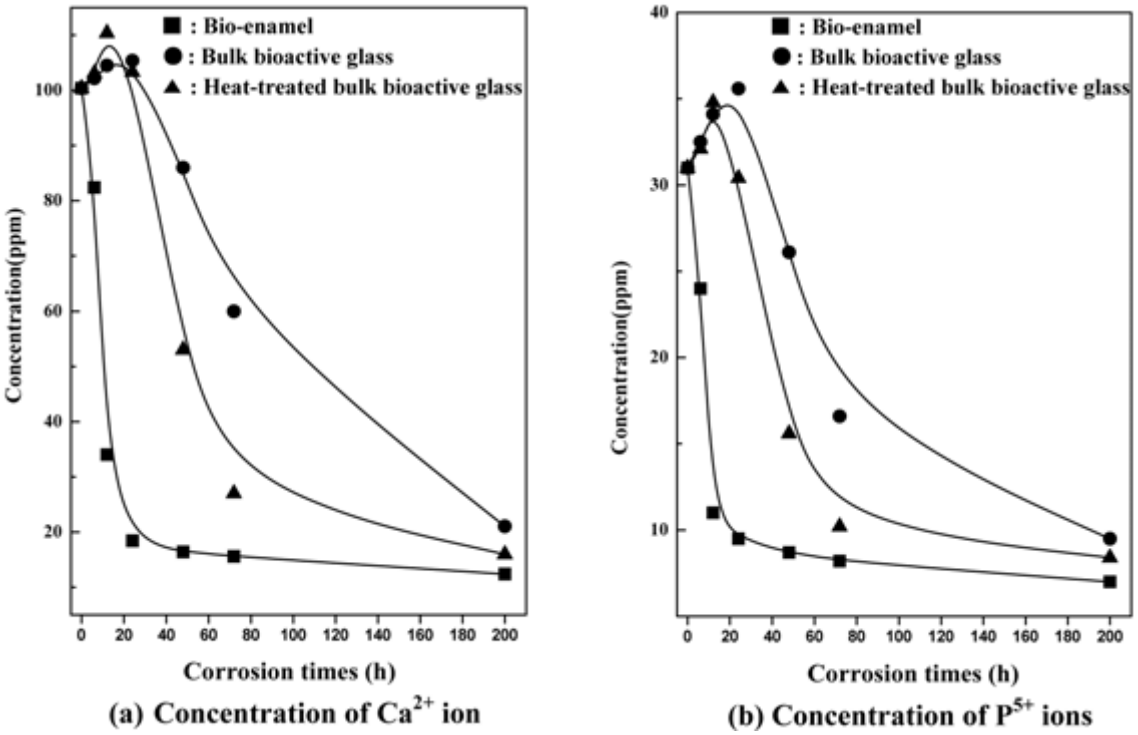

Fig. 8. Ion concentrations of SBF after the reaction with various samples.

A broken piece of silica-rich layer, which was verified by EDS, was observed in the bulk bioactive glass. For the bio-enamel, however, a porous surface without crack was observed, and silicon, calcium, phosphorus and a small amount of sodium were detected by EDX. These ions are the compositional elements of the bioactive glass used in the bio-enamel. This result explains that hydroxyapatite forms more rapidly on bio-enamel without a silica-rich layer which is an essential condition for hydroxyapatite formation on bioactive glass.

Ion concentration remained in simulated body fluids

Figure 8 shows calcium and phosphorus concentrations of the SBF which had been reacted with bio-enamel, heat-treated bioactive glass and bulk bioactive glass.

In the case of the bulk bioactive glass and heat-treated bioactive glass, the amounts of calcium and phosphorus ions were increased slightly at an early stage of reaction because calcium and phosphorus ions in the glass were leached out into the SBF, but the ion concentrations decreased as reaction time passed because those ions were taken up from the SBF to form hydroxyapatite. The reduction of the ion concentrations for the heat-treated bioactive glass is much larger than that for the bioactive glass. This result suggests that the rate of hydroxyapatite formation is much faster in the heat-treated bioactive glass, and this agrees well with the FT-IR results. In the case of the bio-enamel, on the other hand, the concentrations of calcium and phosphorus ions decreased from the beginning of the reaction. It is believed that the calcium and phosphorus ions which leached out of the bio-enamel did not diffuse into the solution but remained around the surface because of the unstable energy state of the surface made by the heat-treatment. These ions trapped on the surface, attracted the Ca^{2+} and P^{5+} ions from the SBF at an initial stage of reaction, and hydroxyapatite started to form from the beginning of reaction.

Conclusions

A bio-enamel was obtained by coating a bioactive glass on titanium metal. To minimize the stress at the interface between the metal and glass, another glass with an intermediate coefficient of thermal expansion was applied underneath the bioactive glass.

Hydroxyapatite formed on the bio-enamel, which was fired at 850 °C for 3 minutes, within 12 hours of reaction in SBF. The rate of hydroxyapatite formation was much faster in the bio-enamel than that in the bioactive glass which had the same composition as the glass used in the bio-enamel. This enhancement of the rate of hydroxyapatite formation also showed up in the heat-treated bioactive glass. The bioactive glass always showed a silica-rich layer before depositing hydroxyapatite, but no silica-rich layer was found in the bio-enamel. This is useful for the application of this material as an implant material because the low strength of the silica-rich layer causes many problems in the practical uses of bioactive glasses.

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