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General paper

BIOMIMETIC COATING OF BONE-LIKE APATITE ON GLASS BEADS

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Abstract: Soda lime glass beads were chemically treated by either an aqueous solution of NaOH (3 mol/l) or a hydrogen peroxide solution (30 vol%) containing $TaCl_5$ in 5×10^{-3} mol/l or by both of them. The treated samples were soaked up to 14 days in a simulated body fluid (SBF): 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, SO_4^{2-} 0.5 (in 10^{-3} mol/l), or in another solution 1.5 times as concentrated as SBF (1.5SBF). The SBFs were kept at 36.5°C and at 7.25 in pH. Apatite was deposited on the samples treated with the NaOH solution, the H_2O_2/Ta solution, and both of them before soaking in 1.5SBF. Ta(V) ions were present on not only the samples treated with the H_2O_2/Ta solution but those treated with both NaOH and the H_2O_2/Ta solutions. It was concluded that Ta(V) ions on the surface layer had ability of inducing apatite deposition, and the ability was enhanced by the coexistence with silanol groups.

Key words: *Apatite, Coating, Glass, Biomimetic process, Chemical treatment, Hydrogen peroxide, Tantalum chloride, X-ray photoelectron spectroscopy, Surface microstructure*

1. INTRODUCTION

Among ceramic materials apatite is applicable as absorbents for blood purification or protein separation since not only it is highly biocompatible with tissues and blood but it shows specific affinity for some proteins or causes of diseases. Current synthetic methods using solid-solid reaction, wet chemical reaction, hydrothermal reaction, or fluxes may give apatite different from bone-apatite in structure and composition because the synthetic reactions proceed under conditions by far different from those in body environment. Biomimetically synthesized apatite, on the other hand, is expected to show better biocompatibility since it is derived under mild conditions simulating body environment. Several ceramics in calcium silicate systems such as Bioglass® [1], Ceravital® [2], or Glass-ceramic A-W [3], to name a few, spontaneously deposit apatite when embedded in the body. Moreover, such materials can deposit bone-like apatite through a series of chemical reactions in a simulated body fluid [4], known as Kokubo solution, that has an inorganic composition similar to human blood plasma. Ohtsuki et al. demonstrated [5] that the calcium ions dissolved from the ceramics enhanced the degree of supersaturation for apatite and thus derived a silica gel layer rich in silanol groups providing nucleating sites of apatite. Thus one may expect deposition of biomimetic apatite layer as in the body when the materials without ability of spontaneous deposition of apatite are covered with such a layer capable of apatite nucleation. Moreover, the compositions and structure of the apatite may depend on the materials, hence one can obtain apatite of wider range of properties.

Osaka and his coworkers found recently [6] that the bone-like apatite was deposited on silicone or titanium metal when treated with $TaCl_5$-containing hydrogen peroxide solutions prior to soaking in Kokubo solution. We thus treated commercially available soda-lime glass beads with a sodium hydroxide solution to provide the silanol groups and the hydrogen peroxide solutions before soaking them in regular or concentrated Kokubo solutions. Then we examined conditions appropriate for the apatite deposition on the beads.

2. EXPERIMENTAL PROCEDURE

An aqueous solution of sodium hydroxide (3 mol/l (=M)) and a hydrogen peroxide solution (30 vol%) containing $TaCl_5$ in 5×10^{-3} M were prepared. They are denoted as 3M NaOH and H_2O_2/Ta later in this report. Soda-lime glass beads (0.1 g), supplied and coded UB-1921L by Union Co., Osaka, with about 1.0 mm in diameter were soaked in the solutions (30 ml) as shown in Table 1. The samples were kept at 60°C for three days in each solution. After rinsed with distilled water and dried in a 40°C oven, the samples were soaked in regular Kokubo solution, denoted as SBF, with composition [4]: 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, SO_4^{2-} 0.5 (in 10^{-3} M). Another solution 1.5 times as concentrated as SBF, denoted as 1.5SBF, was also used for soaking the samples.

Table 1. Chemical treatments and solutions.

Treatments	Solutions	
	1st	2nd
No treatment	—	—
NA	3M NaOH	—
TA	H_2O_2/Ta	—
NATA	3M NaOH	H_2O_2/Ta

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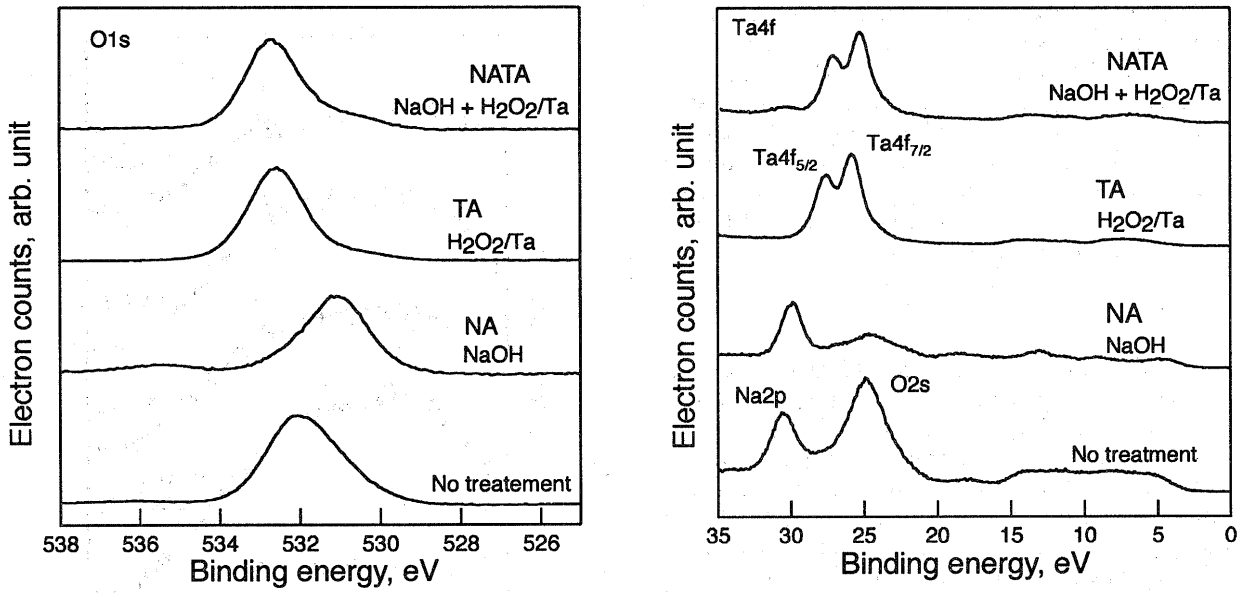

Fig. 1. X-ray photoelectron spectra of the O1s and Ta 4f levels for the glasses after various chemical treatments.

Both solutions were kept at 36.5°C and at 7.25 in pH with Tris buffer. After the soaking up to 14 days, the samples were rinsed and dried.

The surface microstructure of the samples treated above were examined with a scanning electron microscope (SEM) equipped with an energy dispersion X-ray analyser (EDX) and thin-film X-ray diffraction (Cu Kα). X-ray photoelectron spectra (XPS) of O 1s and Ta 4f levels were also taken with Fisons Instruments S-Probe ESCA SSX100S for those before soaking in the SBFs: monochromatic Al Kα X-ray was used and the drift of the peak position due to the surface charge up and chemical shift was controlled as described previously [7]. Inorganic ion concentrations of the SBFs were analyzed with an inductively coupled plasma emission spectrometer (ICP).

3. RESULTS

After SEM observation the NaOH-treated samples (samples NA) had rough surfaces and even pits due to corrosion, while the samples treated with H_2O_2/Ta (samples TA) was similar in surface structure to no-treatment (NT) beads. Figure 1 indicates XPS of O1s and Ta 4f levels for the chemically treated samples. The O 1s peak for sample NT was at about 532 eV corresponding to the bridging (Si-O-Si) oxygen atoms, and the presence of non-bridging (Si-O- Na^+ or Ca^{2+}) oxygen atoms was indicated by a tailing near 530 eV that added scewness to the profile. The peak for sample NA shifted toward lower binding energy (about 531 eV), whereas the peak for sample TA shifted toward higher binding energy (about 533 eV). A similar shift was also found for the samples treated with NaOH and H_2O_2/Ta (sample NATA). A slight hump near 530 eV in the profile for sample NATA suggests the presence of oxygen atoms similar in chemical state to those in sample NA. Figure 1 indicates the presence of Ta on samples TA and NATA that exhibited smooth surfaces irrespective of prior chemical treatment. After soaked in 1.5SBF, samples NT and

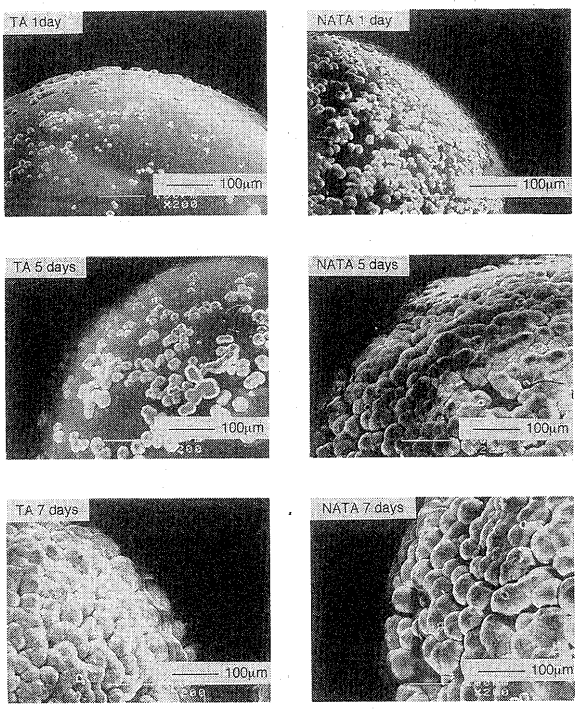

Fig. 2. SEM photographs of samples TA and NATA after soaking on 1.5SBF up to 14 days.

NA had smooth surfaces, whereas samples TA and NATA deposited in a day flaky lumps where EDX analysis detected Ca and P. The lumps covered the whole surface of samples TA and NATA after soaking for 7 days in 1.5SBF. However, larger rate of growth of the lump was noted for sample NATA than for TA since the surface of the former beads was fully covered with the lump within a shorter soaking period (5 days). When soaked in the regular SBF, apatite was never deposited on any samples.

4. DISCUSSION

Figure 3 illustrates thin film X-ray diffraction patterns for the NATA glass beads surface, indicating a peak near 32° in 2θ that corresponds to (211) diffraction of apatite [8]. This strongly suggests that the lumps deposited on the surface of the glass beads was apatite. Figure 4 indicates concentrations of the inorganic ions in the 1.5SBF during the soaking period. Almost no Si was detected in the solution. The decrease in Ca and P for samples TA and NATA corresponds to the deposition of the lump on their surface. Similar decrease is also detected for sample NA, suggesting that similar lumps are deposited. It was noticed that

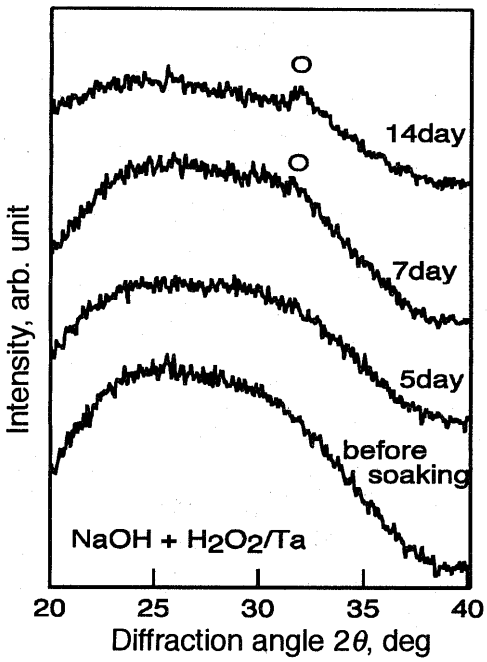

Fig. 3. Thin film X-ray diffraction (Cu Kα) patterns for sample NATA after soaking up to 14 days in 1.5SBF. O: (221) of apatite

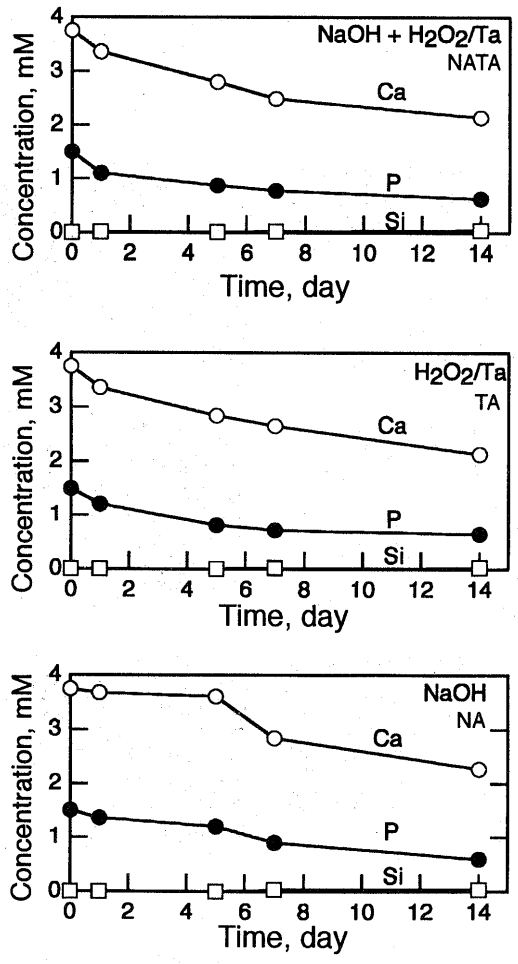

Fig. 4. Ion concentrations of the 1.5SBF for soaking each sample.

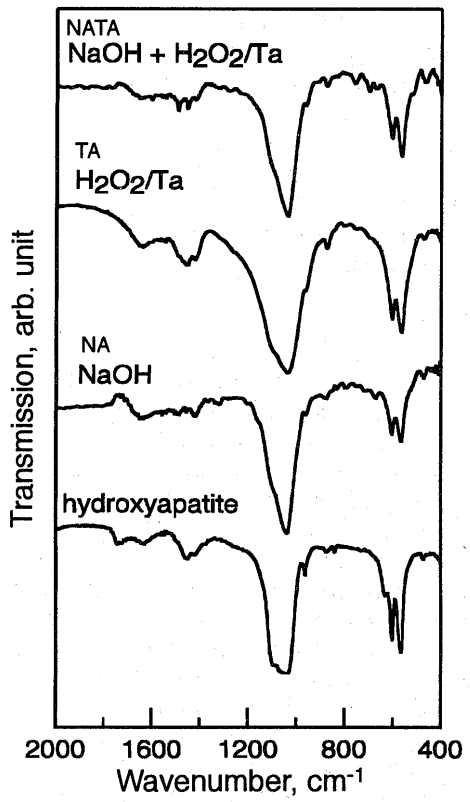

Fig. 5. Infrared spectra of the flakes taken from each sample after soaking in 1.5SBF for 14 days.

many flakes were scattered on the tray on which the beads of sample NA were placed and dried after the 1.5SBF treatment. Thus the surface layers of all the samples were scraped off with a knife. The infrared spectra of the flakes were then taken by the KBr method and were shown in Fig. 5. The spectrum profile for sample NA as well as samples TA and NATA is very similar to that of reagent grade apatite. Therefore, we have concluded that apatite is deposited not only on samples TA and NATA when soaked in 1.5SBF within 1 day but also on sample NA. The apatite layer on sample NA, however, was peeled off due to mechanical shock, suggesting that the adhesion of the apatite layer to the surface was very weak.

When soda-lime glass is in contact with a sodium hydroxide solution, the surface is corroded and a portion of Si-O-Si bridging bonds are dissociated to yield silanol groups, some of which are hydrolyzed into the form of $Si\text{-}O^- \bullet Na^+$ under the highly alkaline condition. With incomplete rinsing the sodium ions remain in the surface layer forming $Si\text{-}O^- \bullet Na^+$ bonds. The oxygen atoms in the bonds give the O 1s peak smaller in binding energy [7], as indicated in Fig. 1. Therefore, a longer induction time for sample NA shown in Fig. 4 is acounted for by the lesser apatite inducing ability of the corroded surface layer rich in Si-O•Na bonds. If apatite is deposited on the layer, the apatite crystallites are likely to be peeled off the glass probably because of insufficient mechanical strength of the surface layer. The TA treatment substitutes protons for the sodium ions on the surface layer of sample NA or on the glass surface of sample NT to yield Si-OH bonds that gives the 533 eV O 1s peak for both samples in Fig. 1. Thus, although sample NA shows smaller ability to deposit apatite, excellent apatite deposition is confirmed for samples TA and NATA in Fig. 2. It is therefore concluded that Ta (V) ions remaining on the surface layer are favorable for inducing the apatite deposition. Moreover, the improved growth of apatite due to the H_2O_2/Ta treatment before soaking the NaOH treated sample in 1.5SBF indicates that the ability of the Ta(V) ions is enhanced by the coexistence with the silanol groups.

5. SUMMARY

Soda lime glass beads were chemically treated by either an aqueous solution of NaOH (3 M) or a hydrogen peroxide solution (30 vol%) containing $TaCl_5$ in 5×10^{-3} M or by both of them. The treated samples were soaked up to 14 days in a simulated body fluid (SBF), known as Kokubo solution (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, SO_4^{2-} 0.5 (in 10^{-3} M)), or in another solution 1.5 times as concentrated as SBF (1.5SBF). The SBFs were kept at 36.5°C and at 7.25 in pH. Surface microstructure was examined by SEM-EDX, XPS, FT-IR, and thin film X-ray diffraction, and the inorganic ion concentrations of the SBFs were analyzed by ICP. Irrespective of chemical treatment, apatite was not deposited on any samples when soaked in SBF. Apatite was deposited on the samples treated with the NaOH solution, the H_2O_2/Ta solution, and both of them before soaking in 1.5SBF. However, adhesion of the apatite layer to the NaOH-treated samples was so weak that it was peeled off the bead surface. Ta(V) ions were detected with XPS on not only the samples treated with the H_2O_2/Ta solution but those treated with both NaOH and the H_2O_2/Ta solutions. Moreover, apatite covered whole surface of the latter samples in shorter period of soaking in 1.5SBF.

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