The Korean Journal of Ceramics, 4 [4] 336 - 339 (1998)

Mechanism of Apatite Formation on Bioactive Titanium Metal

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(Received September 23, 1998)

Bioactive titanium metal can be prepared by simple 5M-NaOH treatment and subsequent heat treatment at 600°C to form an amorphous sodium titanate on its surface. In the present study, mechanism of apatite formation on the titanium metal was investigated by examining its surface compositional and structural changes in a simulated body fluid. The apatite formation on the metal was found to proceed in the sequence of 1) Na^+ ion release from the sodium titanate to form hydrated titania abundant in Ti-OH groups, 2) early and selective binding of calcium ions with the Ti-OH groups to form a calcium titanate, and 3) late binding of phosphate ions to make apatite nucleation and growth. This indicates that Ti-OH groups do not directly induce the apatite nucleation, but via formation of a calcium titanate.

Key words : Titanium (Ti), Chemical treatment, Bioactivity, Apatite, Simulated body fluid (SBF)

I. Introduction

The present authors recently showed that bioactive titanium metal can be prepared by simply subjecting the metal to NaOH and subsequent heat treatments to form an amorphous sodium titanate on its surface.[1] The bioactive metal thus obtained bonds to and integrates with living bone via formation of a biologically active bonelike apatite layer on its surfaces in the body, as the bioactive ceramics do.[2] This type of bioactive metals are believed to be useful as bone substitutes even under load-bearing conditions, since they are not only intrinsically tough but also able to tightly bone to living bone.

The authors attributed the apatite formation on the metal to a specific surface structure of the sodium titanate formed by the NaOH and heat treatments; the sodium titanate was speculated to transform into a hydrated titania to induce apatite formation after being exposed to body environment.[1,3] Details on how the apatite could be formed on the metal is, however, not clear yet. In the present study, the mechanism of apatite formation on the bioactive titanium metal was investigated in a simulated body fluid with pH and ion concentrations nearly equal to those of human blood plasma.

II. Experimental Procedure

Commercially pure titanium (Ti; Ti>99.8%, Kobe Steel Ltd., Japan) substrates $10\times10\times1$ mm^3 in size, whose surfaces were abraded with No. 400 diamond plate, were soaked in 5.0M-NaOH aqueous solution at 60°C for 24 h, gently washed with distilled water, and dried at 40°C for 24 h in air atmosphere. They were then heated up to 600°C at a rate of 5°C/min in an electrical furnace, kept at 600°C for 1 h, and allowed to cool in the furnace. The Ti substrates thus treated were soaked in 24 mL of an acellular simulated body fluid (SBF) with pH (7.40) and ion concentrations (Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, SO_4^{2-} 0.5 mM) nearly equal to those of human blood plasma at 36.5°C. The SBF was prepared by dissolving reagent grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4\cdot3H_2O$, $MgCl_2\cdot6H_2O$, $CaCl_2$ and Na_2SO_4 into distilled water, and buffered at pH 7.40 with tris-hydroxymethyl-aminomethane ($(CH_2OH)_3CNH_3$) and hydrochloric acid at 36.5°C.[4] After soaking for various periods up to 7 d, the substrates were removed from the SBF, washed with distilled water, and dried in a clean bench. The SBF was early proposed by Kokubo *et al.* and has been extensively confirmed to reproduce the *in vivo* bonelike apatite formations on bioactive materials.[5-8]

Surfaces of the Ti substrates after the NaOH and heat treatments and subsequent soaking in SBF were analyzed by scanning electron microscopy (SEM; Model S2500CX, Hitachi Co., Japan), thin-film X-ray diffraction (TF-XRD; Model 2651A1, Rigaku Co., Japan) and X-ray photoelectron spectroscopy (XPS; Model MT5500, ULVAC-PHI Co., Japan). Element concentrations and pH of the SBF after soaking of the substrates were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP; Model SPS1500, Seiko Inst. Co., Japan) and elec-

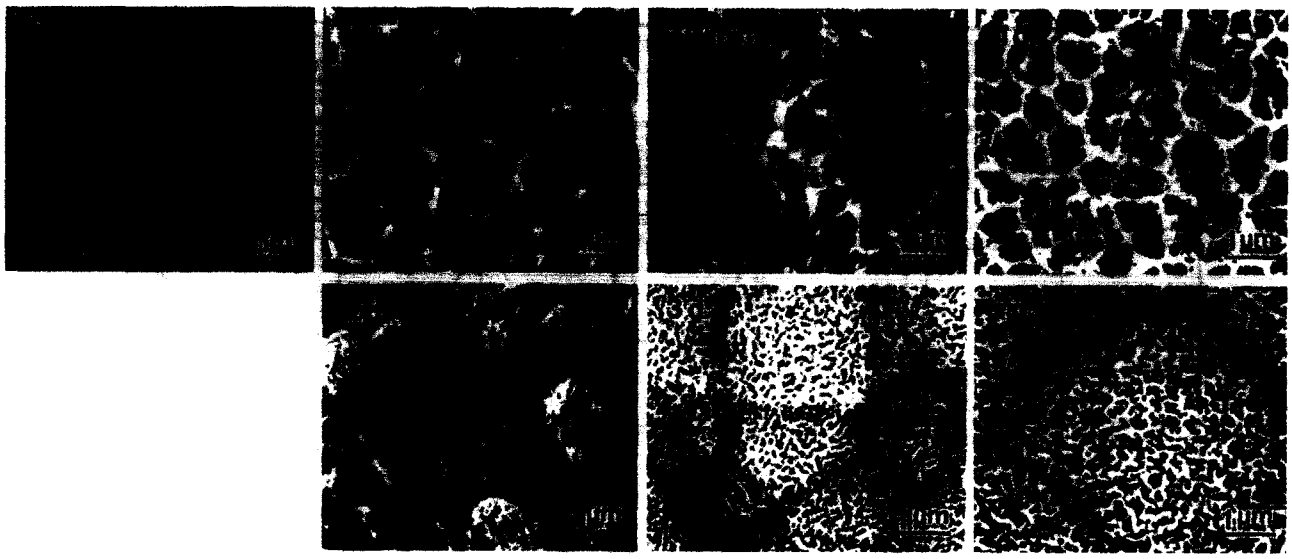

Fig. 1. SEM photographs of the surfaces of Ti substrates before (BT) and after the NaOH and heat treatments (AT) and subsequent soaking in SBF for various periods.

trolyte-type pH meter (Model D-14, Horiba Co., Japan).

III. Results and Discussion

Fig. 1 and 2 show SEM photographs and TF-XRD patterns of the surfaces of Ti substrates before (BT) and after the NaOH and heat treatments (AT) and subsequent soaking in SBF for various periods. A porous network surface structure was observed to be formed on the Ti substrate after the NaOH and heat treatments. Corresponding XRD pattern indicates that this surface layer is an amorphous sodium titanate containing small amounts of crystalline sodium titanate ($Na_2Ti_5O_{11}$) and rutile (TiO_2). After soaking in SBF for 2 d, some spherulite crystals were observed to be deposited on the Ti substrate. They gradually grew to cover the whole surface of substrate with further increase in soaking time. XRD peaks newly appeared after soaking in SBF were all ascribed to crystalline apatite, indicating that the spherulites are assemblies of tiny apatite crystals.

Fig. 3 shows Na_{1s}, Ca_{2p}, P_{2p} and O_{1s} XPS spectra of the surfaces of Ti substrates before (BT) and after the NaOH and heat treatments (AT) and their changes as a function of soaking time in SBF. The Na1s spectrum was a single peak at binding energy of 1072.4±0.1 eV. The Na_{1s} spectrum is due to the sodium titanate formed on the Ti substrate by the NaOH and heat treatments. The peak intensity gradually decreased to completely disappear in soaking time up to 2 d. The Ca_{2p} spectra were a doublet peak at binding energies of $Ca_{2p1/2}$=350.6±0.4 eV and $Ca_{2p3/2}$=347.1±0.3 eV. The Ca_{2p} spectrum was first detected as early as within 30 min after the immersion and to abruptly increase its intensity after 2 d, at which the peak position at half maximum binding energy slightly shifted to a lower binding energy. It should be also noted

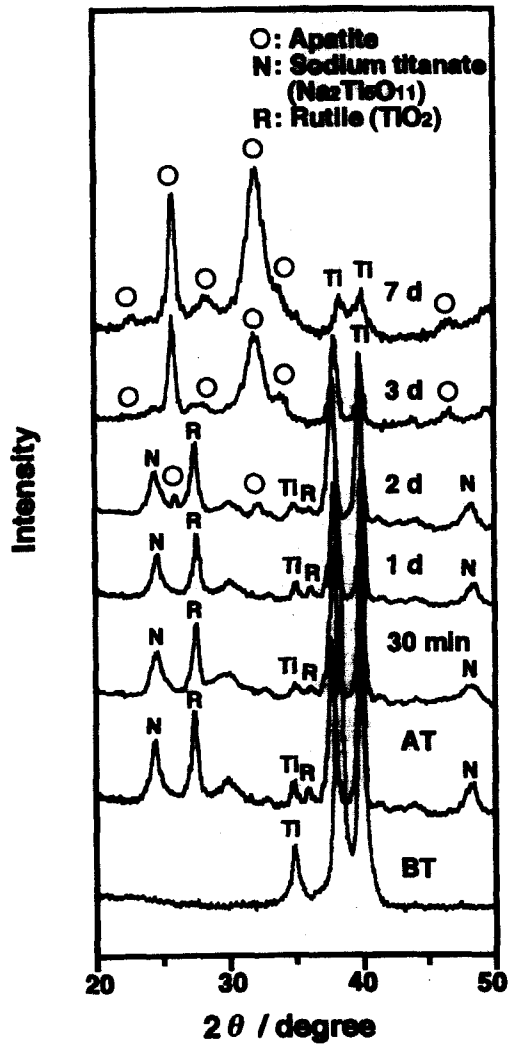

Fig. 2. TF-XRD patterns of the surfaces of Ti substrates before (BT) and after the NaOH and heat treatments (AT) and subsequent soaking in SBF for various periods.

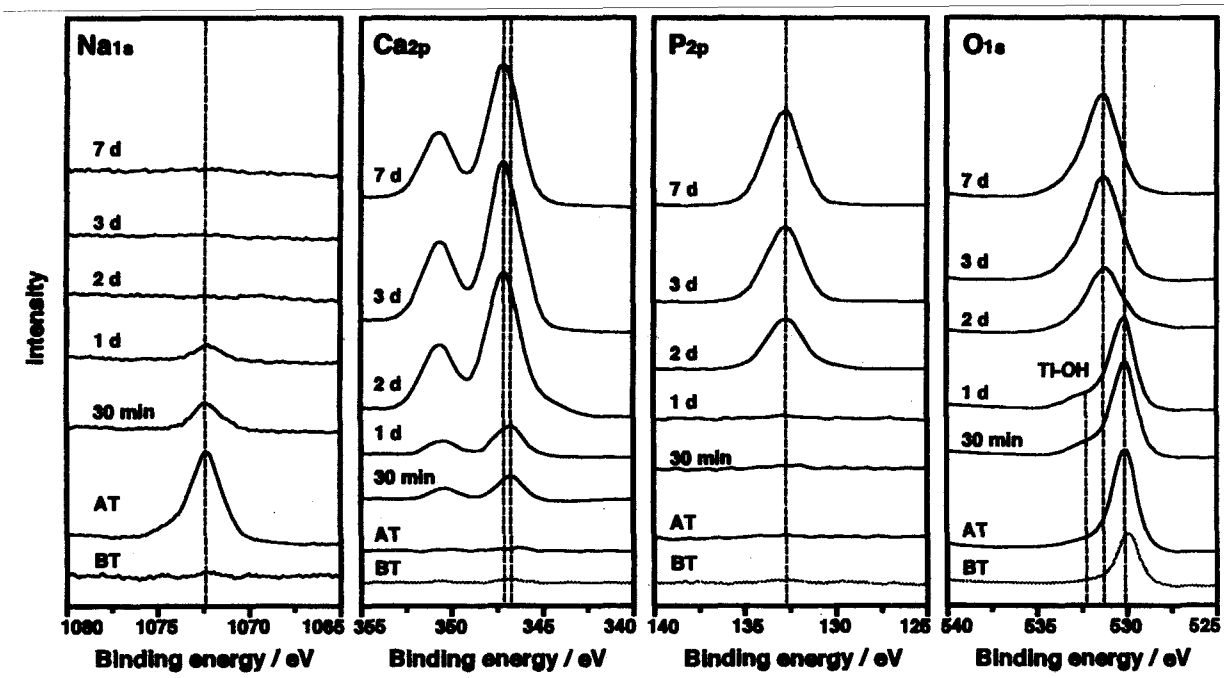

Fig. 3. Na1s, Ca_{2p}, P_{2p} and O1s XPS spectra of the surface of Ti substrate before (BT) and after the NaOH and heat treatments (AT) and their changes as a function of soaking time in SBF.

that apatite crystals were first observed around this time (Figs. 1 and 2). The P_{2p} spectrum was a single peak at binding energy of 132.6±0.1 eV. The P_{2p} spectrum was detected about 2 d later than the Ca_{2p} spectrum. This time coincided with the time when the intensity of Ca_{2p} spectrum abruptly increased and the apatite crystals were first observed (Figs. 1 and 2). The O_{1s} spectrum was a single peak including a shoulder peak. The main peak at binding energy of 530.3±0.1 eV represents the oxygen bonded to the titanium.[9,10] The shoulder peak appeared at a higher binding energy after soaking in SBF is ascribed to Ti-OH groups.[11] After soaking in SBF for 2 d, the peak position shifted to a higher binding energy of 531.3±0.1 eV. This peak may represent phosphate in the apatite on the surface of the Ti substrate, since the time of peak shift also coincided with the time of the first detection of the apatite.

Fig. 4 shows changes in pH and Na, Ca, and P concentrations of SBF with soaking of the Ti substrate subjected to the NaOH and heat treatments. Early event occurred in SBF due soaking of the Ti substrates was simultaneous and rapid increases in Na concentration and pH, indicating that the substrates released Na^+ ion from the surface sodium titanate via ion exchange with H_3O^+ ion in the fluid. Gradual decreases in Ca and P concentrations was followed to proceed for a long period of soaking due to apatite formation. All these changes corresponded well to the results shown in Figs. 1 to 3.

Compositional and structural changes of the surface of Ti substrate subjected to the NaOH and heat treatments as a function of soaking time in SBF were represented in

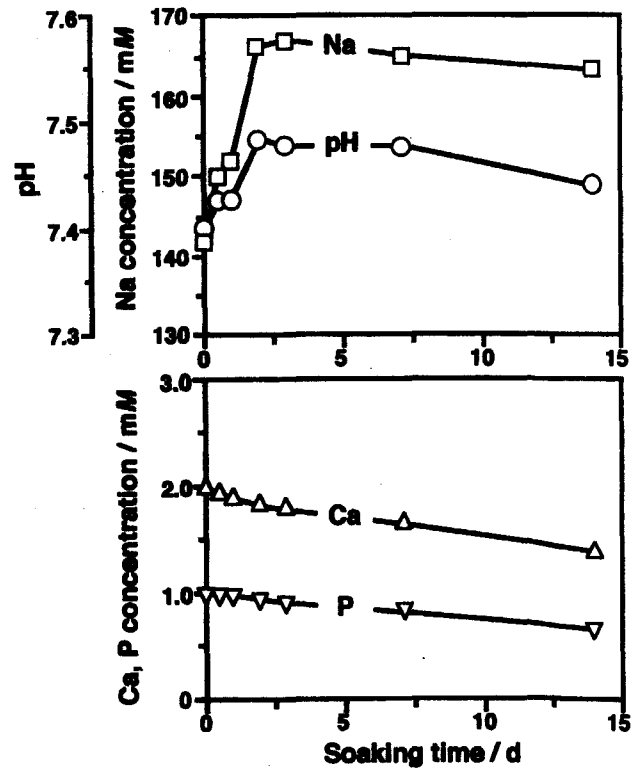

Fig. 4. Changes in pH and Na, Ca, and P concentrations of SBF with soaking of the Ti substrate subjected to the NaOH and heat treatments.

Fig. 5 upon the basis of the above results. Although formations of hydrated titania and calcium titanate could not be directly known in the present study,

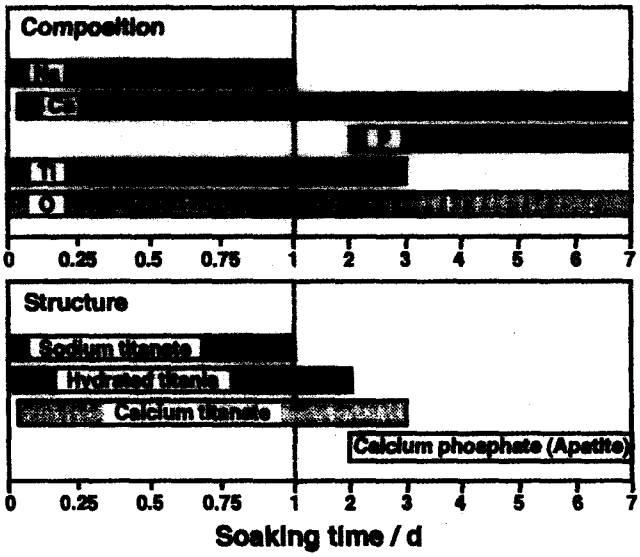

Fig. 5. Compositional and structural changes of the surface of Ti substrate subjected to the NaOH and heat treatments as a function of soaking time in SBF.

compositional changes and peak shifts shown in Fig. 3 indicate that they do involve prior to the apatite formation. Phase revelation on the surface of Ti substrate with soaking time in SBF is therefore assumed to be occur in the sequence of sodium titanate, hydrated titania, calcium titanate and then apatite.

Previously, apatite nucleation on the above bioactive Ti metal was assumed to merely be induced by Ti-OH groups in a hydrated titania formed via Na^+ ion release from the sodium titanate.[1,3,12] The above results, however, indicates that the apatite formation involves some intermediate steps. The apatite formation is speculated to proceed in the sequence of 1) Na^+ ion release from the sodium titanate to form hydrated titania abundant in Ti-OH groups, 2) early and selective binding of calcium ions with the Ti-OH groups to form a calcium titanate, and 3) late binding of phosphate ions to make apatite nucleation and growth. Namely, the apatite nucleation is speculated to be induced not directly by Ti-OH groups, but via formation of a calcium titanate.

VI. Conclusions

The Ti-OH groups, which are formed on bioactive Ti metal via exchange of Na^+ ion in the surface sodium titanate layer with the H_3O^+ ion in SBF, combined with only the calcium ion as early as within 30 min, and then with the phosphate ion 2 days later to form the apatite. This indicates that Ti-OH groups do not induce the apatite nucleation directly, but via formation of a calcium titanate.

Acknowledgments

This study was supported by Grant-in-Aid for Scientific Research, the Ministry of Education, Science, Sports, and Culture, Japan.

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