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Effect of heat treatment on apatite-forming ability of Ti metal induced by alkali treatment

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The present authors previously showed that titanium metal forms a bone-like apatite layer on its surface in a simulated body fluid (SBF), when it has been treated with a NaOH solution to form a sodium titanate hydrogel layer on its surface. This indicates that the NaOH-treated Ti metal bonds to living bone. The gel layer as-formed is, however, mechanically unstable. In the present study, the NaOH-treated Ti metal was heat treated at various temperatures in order to convert the gel layer into a more mechanically stable layer. The gel layer was dehydrated and transformed into an amorphous sodium titanate layer at 400–500 °C, fairly densified at 600 °C and converted into crystalline sodium titanate and rutile above 700 °C. The induction period for the apatite formation on the NaOH-treated Ti metal in SBF increased with the transformation of the surface gel layer by the heat treatment. Ti metal heat treated at 600 °C, however, showed a fairly short induction period as well as high mechanical stability, since it was covered with a fairly densified amorphous layer.

1. Introduction

A large number of processes for coating bioactive ceramics such as hydroxyapatite onto metals such as stainless steel and titanium alloys have been proposed for obtaining tough bioactive materials usable as bone substitutes even under highly loaded conditions such as hip joints [1–11]. Among them, titanium alloys coated with hydroxyapatite by a plasma spray method is already clinically used [1, 4–6]. In this technique, however, hydroxyapatite powder is momentarily heated over 10 000 °C, and partially molten particles are deposited on the metals. Therefore, it is difficult to control the composition and crystallinity of the hydroxyapatite. The resultant hydroxyapatite layer is porous and weakly bonded to the metallic substrate, and hence, not stable for a long period in the living body [3, 12–23].

It is already known that the essential requirement for an artificial material to bond to living bone is the formation of a bone-like apatite layer on its surface in the body environment [24–28]. The bone-like apatite formation on bioactive ceramics can be reproduced even in an acellular simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma [29, 30]. The present authors previously showed that titanium metal also forms the bone-like apatite layer on its surface in SBF, when it has been previously treated with NaOH aqueous solution to form a sodium titanate hydrogel layer on its surface [31, 32]. Thus it is expected that alkali-treated titanium metal could also form the bone-like apatite layer on its surface in the living body and bond to living bone through the apatite layer. The gel layer as-formed by the alkali treatment is, however, not mechanically stable, and hence, the alkali-treated titanium metal is not suitable for clinical applications.

In the present study, the alkali-treated titanium metal was subjected to various heat treatments in order to stabilize the gel layer. Effects of the heat treatment on the apatite-forming ability of the alkali-treated titanium metal was examined in SBF. The result was discussed in terms of the surface structural change of the alkali-treated titanium metal by the heat treatment.

2. Experimental procedure

2.1. Alkali and heat treatments of Ti metal

Commercially pure titanium (Ti) plates $10 \times 10 \times 1$ mm^3 in size (Ti > 99.8%, Kobe Steel Co. Ltd., Kobe, Japan) were abraded with no. 400 diamond paste, and washed with pure acetone and distilled water in an ultrasonic cleaner. They were treated with 5.0 M NaOH aqueous solution at 60 °C for 24 h, washed gently with distilled water and dried at 40 °C for 24 h. Then, the metal plates were heated up to various

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temperatures ranging from 400 to 800 °C at a rate of $5\,^{\circ}\mathrm{C\,min^{-1}}$ in SiC furnace, kept at the desired temperature for 1 h and allowed to cool in the furnace.

2.2. Soaking of Ti metal in SBF

The Ti specimens subjected to the NaOH and subsequent heat treatments were soaked in an acellular simulated body fluid (SBF) with pH and ion concentrations nearly equal to those of human blood plasma, as given in Table I. The SBF was prepared 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 into distilled water, and buffered at pH 7.40 with tris(hydroxymethyl)amminomethane ($(CH_2OH)_3CNH_3$) and hydrochloric acid at 36.5 °C. Each specimen was soaked in 25 ml of SBF at 36.5 °C for various periods, and then removed from the fluid and washed with pure acetone.

2.3. Analyses of specimen surface and SBF

Surface structural changes of the specimens due to the NaOH and heat treatments and the subsequent soaking in SBF were analysed by laser Raman spectroscopy (Model T64000, ISA JOBIN YVON, France), thin-film X-ray diffraction (TF-XRD: Model 2651A1, Rigaku, Japan) and scanning electron microscopy (SEM: Model S2500CX, Hitachi, Japan). Changes in pH and element concentrations of SBF due to the soaking of the specimens were analysed by pH meter (Model D-14, Horiba, Japan) and inductively coupled plasma (ICP) atomic emission spectroscopy (Model S2500CX, Hitachi, Japan), respectively.

TABLE I Ion concentrations and pH of simulated body fluid (SBF) and those of human blood plasma

Ion	Concentration (mM)	
	SBF	Blood plasma
Na^+	142.0	142.0
K^+	5.0	5.0
Mg^{2+}	1.5	1.5
Ca^{2+}	2.5	2.5
Cl^-	147.8	103.8
HCO_3^-	4.2	27.0
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5
pH	7.40	7.20–7.40

3. Results

Fig. 1 shows the SEM photographs of the surfaces of NaOH-treated Ti metals subjected to heat treatments at various temperatures. It can be seen from Fig. 1 that a porous network structure is formed on the surface of Ti metal by the NaOH treatment and starts to densify eliminating pores around 600 °C. The porous network structure was attributed to a gel layer in the previous paper [32].

Fig. 2 shows the SEM photographs of the surfaces of the Ti metal as-treated with the NaOH solution and that subsequently heat treated at 600 °C, half of which were stuck to and detached with Scotch® tape. It can be seen from Fig. 2 that the porous network gel layer of the surface of the Ti metal as-treated with the NaOH solution is so weak that it is completely peeled off by the tape, while the surface layer of that subsequently heat treated at 600 °C is so strong that it did not peel off but captured the glue of the tape.

Fig. 3 shows the TF-XRD patterns of the surfaces of the NaOH-treated Ti metals subjected to heat treatments at various temperatures. Assignments of the main diffraction peaks are given in Fig. 3. Broad diffraction peaks newly appeared around 23–29 ° and 48 ° in 2 θ after the NaOH treatment. These peaks were attributed to the sodium titanate hydrogel layer

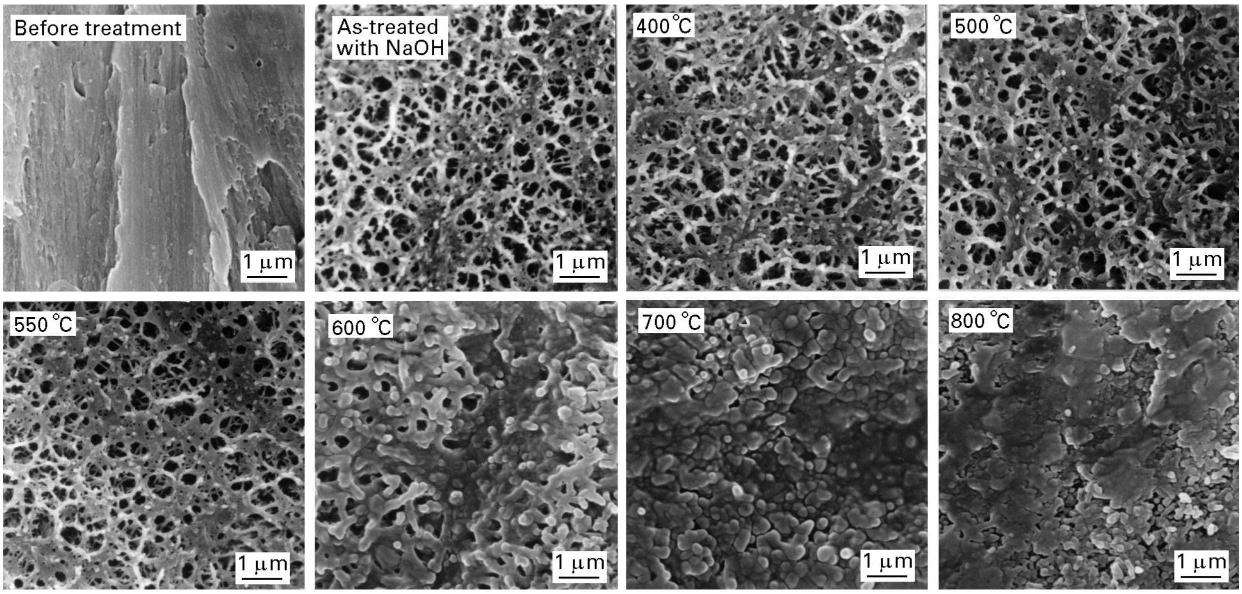


Figure 1 SEM photographs of the surfaces of the NaOH-treated Ti metals subjected to heat treatments at various temperatures, in comparison with that of Ti metal before treatment.

in the previous paper [32]. It can be seen from Fig. 3 that the gel layer starts to precipitate crystalline sodium titanate ($Na_2Ti_5O_{11}$) and rutile (TiO_2) around 600 °C and fully crystallizes above 700 °C.

Fig. 4 shows the Raman spectra of the surfaces of the NaOH-treated Ti metals subjected to heat treatments at various temperatures. Five broad peaks appeared after the NaOH treatment. The peak at

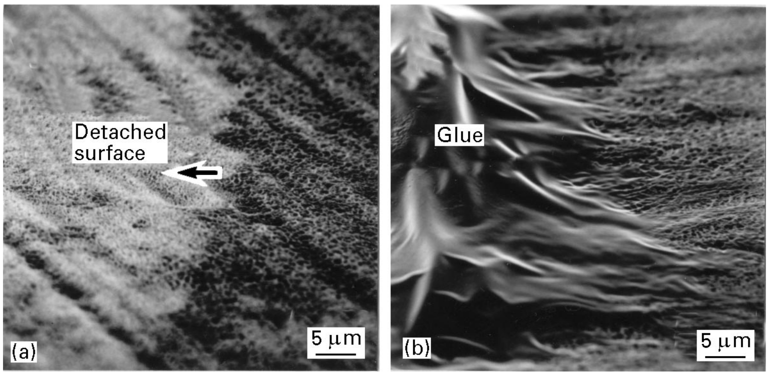


Figure 2 SEM photographs of the surfaces of Ti metal (a) as-treated with the NaOH solution and that (b) subsequently heat-treated at 600 °C. Left hand sides of their surfaces were stuck to and detached with Scotch® tape.

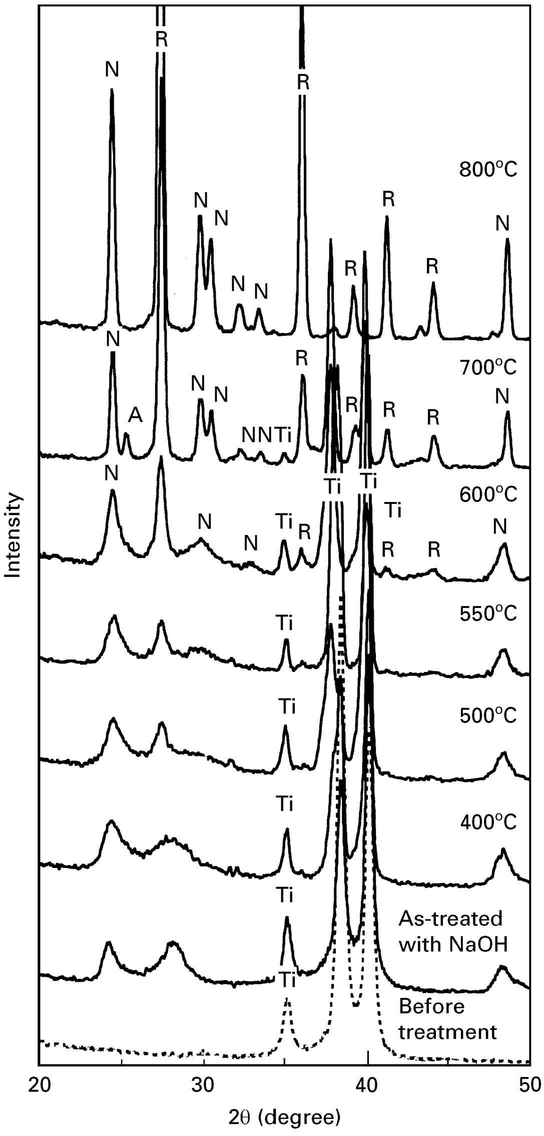


Figure 3 TF-XRD patterns of the surfaces of the NaOH-treated Ti metals subjected to heat treatments at various temperatures (R = rutile; A = anatase; N = $Na_2Ti_5O_{11}$).

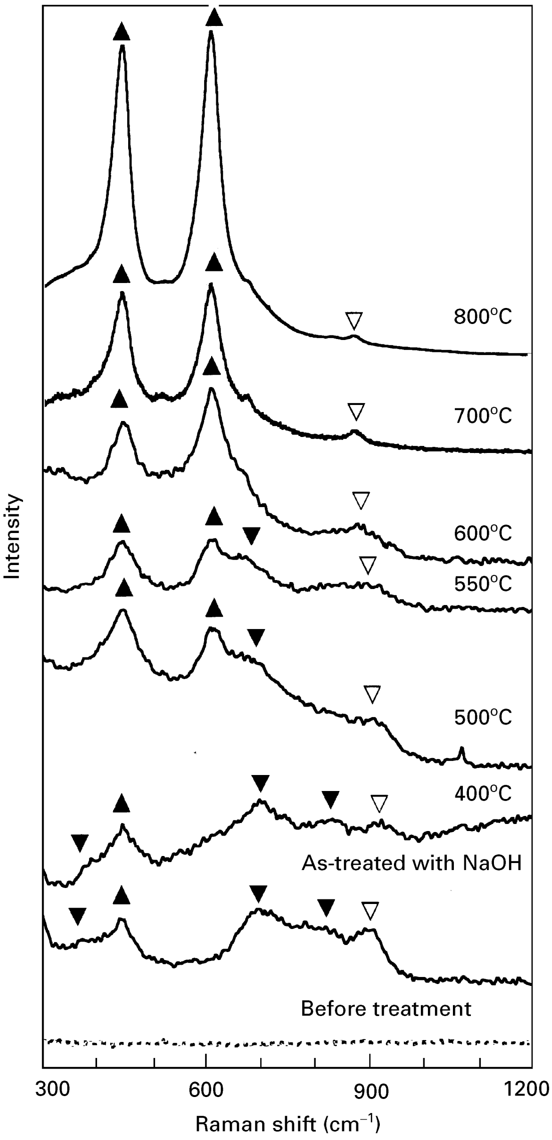
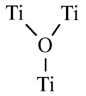


Figure 4 Raman spectra of the surfaces of the NaOH-treated Ti metals subjected to heat treatments at various temperatures (∇: Ti–O, ▼: Ti–O–Ti, ▲:



$\overset{Ti\quad Ti}{\underset{Ti}{O}}$).

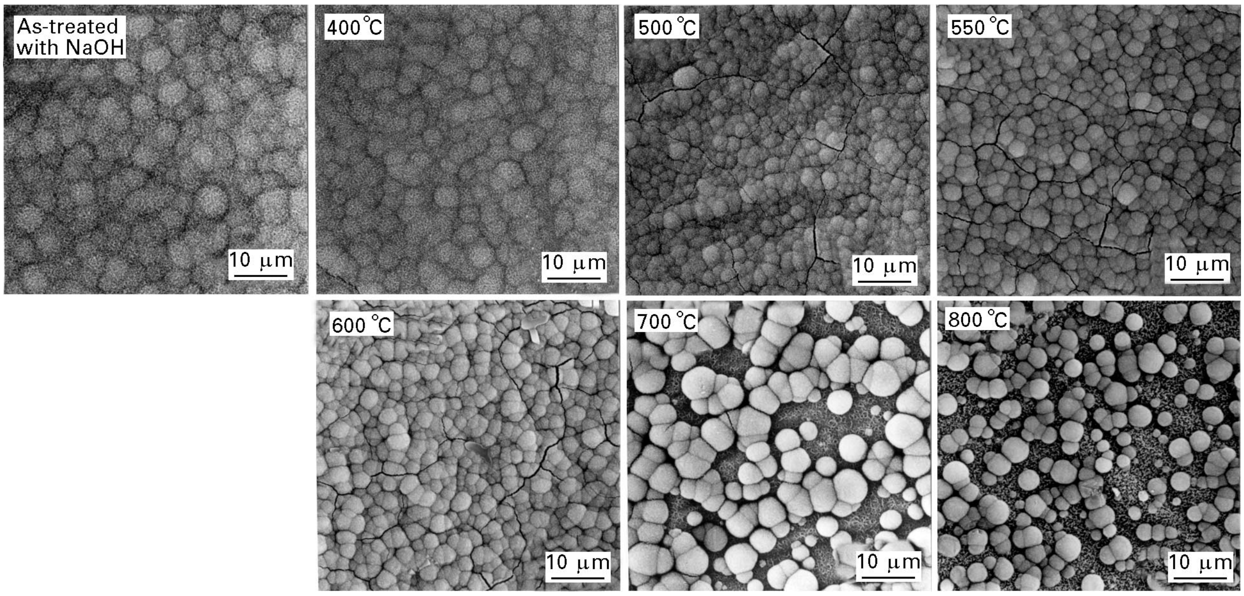


Figure 5 SEM photographs of the surfaces of the NaOH-treated Ti metals which were soaked in SBF for 7 d after heat treatments at various temperatures.

about 440 cm^{-1} is assigned to Ti–O bending vibration involving three-fold oxygen; the peaks at about 380, 690 and 810 cm^{-1} to Ti–O bending and stretching vibration involving two-fold oxygen; the peak at about 905 cm^{-1} to Ti–O stretching vibration involving non-bridging oxygen, some of which are coordinated with Na$^+$ ions [33–36]. All these peaks were attributed to the sodium titanate hydrogel layer in the previous paper [32]. Among them, the peaks at 380, 690 and 810 cm^{-1}, ascribed to Ti–O bending and stretching vibration involving two-fold oxygen disappeared on heat treatment above 500 °C, and a peak assigned to Ti–O stretching vibration involving three-fold oxygen newly appeared at about 600 cm^{-1}. This new peak and the peak at 440 cm^{-1} ascribed to Ti–O bending vibration involving three-fold oxygen increased in their intensities with increasing heat treatment temperature, especially above 700 °C. These spectral changes are ascribed to a structural stabilization of the open network structure of the hydrogel into a dehydrated three-dimensional one, with titanium of six-fold coordination and oxygen of three-fold coordination, by the heat treatment [36]. Broad peaks of the specimen heat-treated at 600 °C indicate that the surface layer still remains essentially as an amorphous phase.

Fig. 5 shows the SEM photographs of the surfaces of the NaOH-treated Ti metals which were soaked in SBF for 7 d after heat treatments at various temperatures. It can be seen from Figs 1 and 4 that spherical particles are deposited on the surface of the Ti metal after soaking in SBF. The density of the spherical particles decreased with increasing heat treatment temperature above 700 °C.

Fig. 6 shows the TF-XRD patterns of the surfaces of the NaOH-treated Ti metals which were soaked in SBF for 7 d after heat treatments at various temperatures. It can be seen from Fig. 6 that all the Ti metals form the apatite on their surfaces in SBF within 7 d. The amount of the apatite, however, decreases

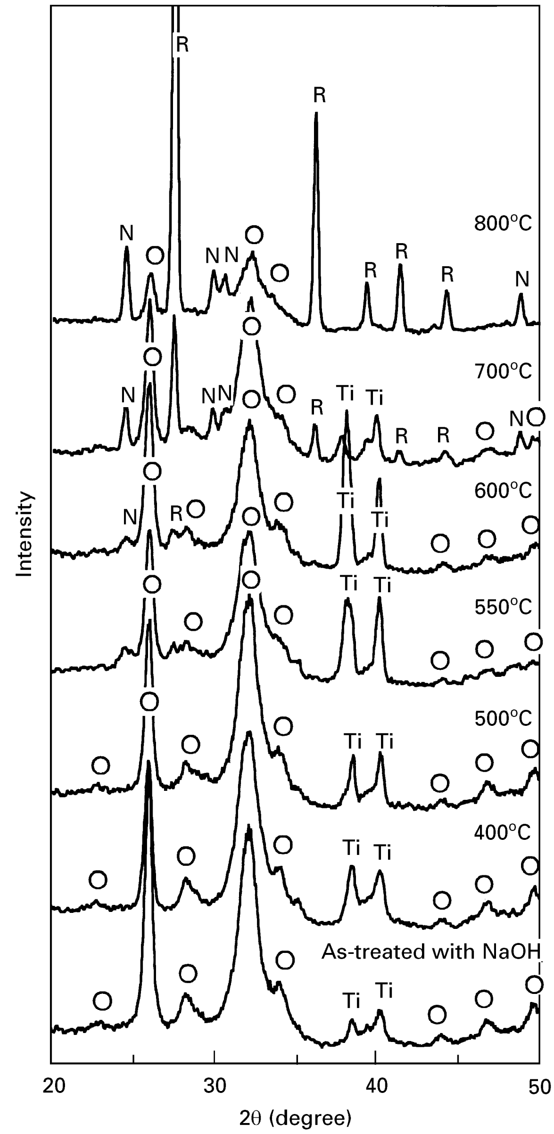


Figure 6 TF-XRD patterns of the surfaces of the NaOH-treated Ti metals which were soaked in SBF for 7 d after heat treatments at various temperatures (O = apatite; R = rutile; N = $Na_2Ti_5O_{11}$).

with increasing heat treatment temperature above 700 °C.

Table II shows the apatite formation on the NaOH-treated Ti metals subjected to heat treatments at various temperatures, as a function of soaking time in SBF. It can be seen from Table II that the induction period for apatite formation increases from 1 to 3 days on heat treatment at 400 °C, but does not increase further following those in the range 400 to 600 °C, and again increases to 7 days following those above 700 °C.

Fig. 7 shows the changes in pH and element concentrations of SBF with soaking of the NaOH-treated Ti metals subjected to no heat treatment and those at 600

TABLE II Apatite formation on the surfaces of the NaOH-treated Ti metal subjected to heat treatments at various temperatures, as a function of soaking time in SBF

Heat treatment	Apatite formation in SBF					
	0.5 d	1 d	3 d	7 d	14 d	28 d
None	—	○	○	○	○	○
400 °C	—	—	○	○	○	○
500 °C	—	—	○	○	○	○
550 °C	—	—	○	○	○	○
600 °C	—	—	○	○	○	○
700 °C	—	—	—	○	○	○
800 °C	—	—	—	○	○	○

—: Apatite was not detected by TF-XRD.
○: Apatite was detected by TF-XRD.

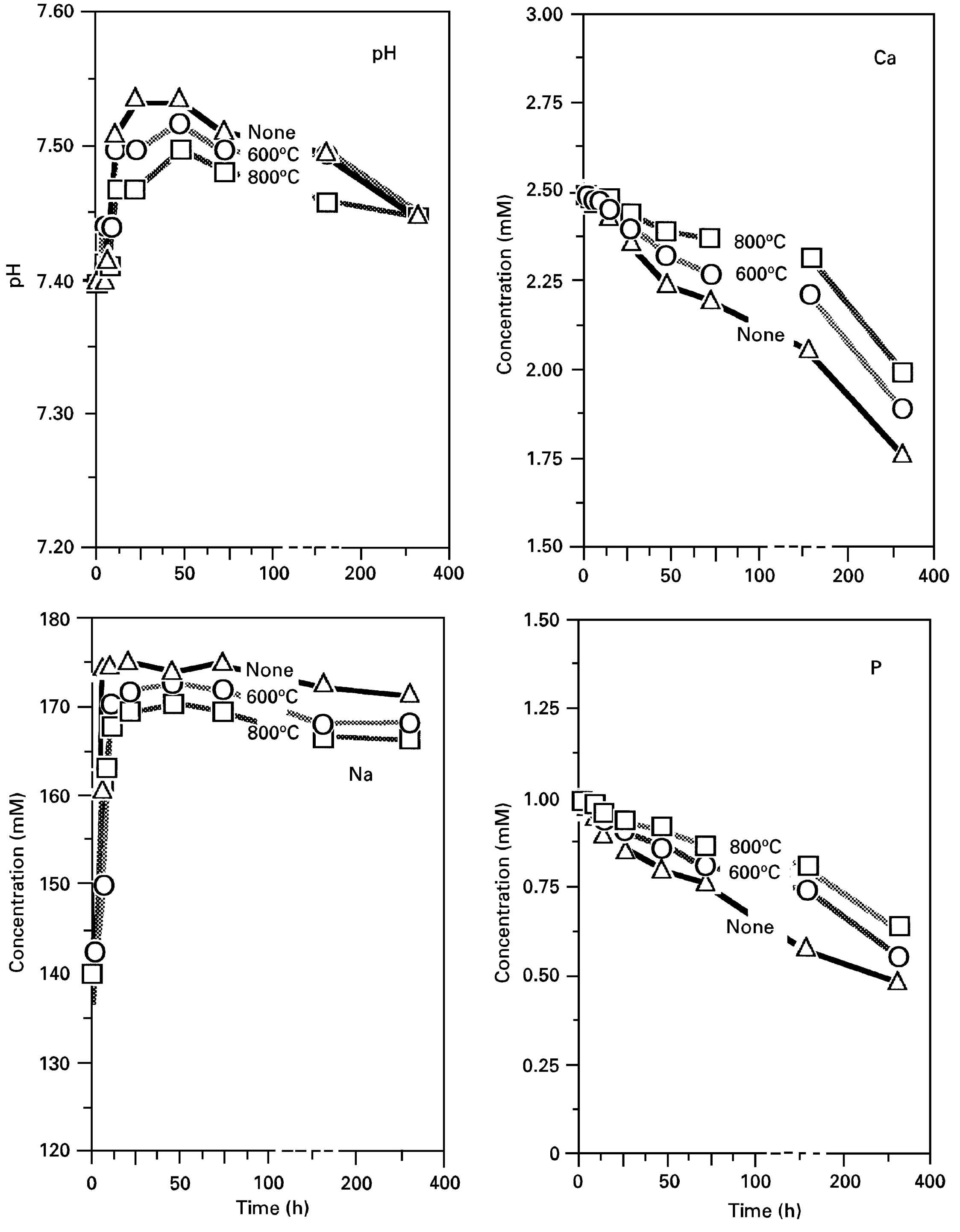


Figure 7 Changes in pH and element concentrations of SBF with soaking of the NaOH-treated Ti metals subjected to no heat treatment and those at 600 and 800 °C.

and 800 °C. All the Ti metal gave rapid increase in Na concentration and pH in early stage up to about 24 h, and gradual decreases in Ca and P concentrations lasted for a long period. The rates of these changes decreased with increasing heat treatment temperature.

3. Discussion

It is apparent from the results described above that the porous sodium titanate hydrogel layer which is formed on the surface of Ti metal by the NaOH treatment is densified and stabilized as a mechanically strong essentially amorphous sodium titanate layer containing a small amount of crystalline sodium titanate and rutile following a heat treatment around 600 °C. Although the induction period for the apatite formation on the surface of the NaOH-treated Ti metal in SBF increases by a heat treatment, its increase is not considerable when the temperature of the heat treatment is around 600 °C. Such dependence of the induction period for the apatite formation on the heat treatment is interpreted in terms of the surface structural changes of the Ti metals as follows.

When exposed to SBF, the NaOH-treated Ti metal releases the Na^+ ion from its surface sodium titanate hydrogel layer into the SBF via exchanges for H_3O^+ ion in the fluid. As a result, pH of the fluid increases, and almost simultaneously, a hydrated titania is formed on the surfaces of Ti metal. The hydrated titania induces the apatite nucleation, as proved for sol–gel derived TiO_2 hydrogel [37, 38], and the pH increase accelerates the apatite nucleation by increasing the ionic activity product of apatite in SBF [39]. A large number of apatite nuclei are thus formed on the surface of the Ti metal. Once the apatite nuclei are formed, they spontaneously grow by consuming the calcium and phosphate ions from the surrounding fluid, since SBF is already highly supersaturated with respect to the apatite even before the soaking of the metals [40, 41]. When the NaOH-treated Ti metal is subjected to a heat treatment, its surface sodium titanate hydrogel layer is dehydrated and transformed into an amorphous sodium titanate at 400 to 500 °C, fairly densified at 600 °C and then converted into crystalline sodium titanate and rutile above 700 °C. The rate of the Na^+ ion release from the surface layer decreases with the structural change from the gel to amorphous phase and then crystalline phases (see Fig. 7). Therefore, the rates of formation of the hydrated titania on the surface of the Ti metal and the increase in pH of the surrounding fluid decrease. As a result, the induction period for the apatite formation decreases. The decrease in the Na^+ ion release rate with the transformation from the amorphous phase to crystalline phases is remarkable, and hence the increase in the induction period for the apatite formation is also remarkable. The surface layer of the NaOH-treated Ti metal subjected to a heat treatment at 600 °C is fully dehydrated and fairly densified, but still remained essentially as amorphous phase. Therefore, it gives a fairly short induction period for the apatite nucleation, i.e. 3 days. This induction period is comparable to that of highly bioactive glass-ceramic A-W [26–30].

It is believed that not only the Ti metal subjected only to the NaOH treatment, but also that subjected to the subsequent heat treatment at 600 °C form the apatite layer spontaneously on their surfaces in the living body and bond to bone through the apatite layer. From a practical point of view, the latter material might be more useful, because it shows a higher mechanical surface stability without giving an appreciable decrease in its bioactivity. This is believed to be useful as a bone substitute even under load bearing conditions.

4. Conclusions

Titanium metal shows a fairly high apatite-forming ability in a body environment, and hence bone-bonding ability, as well as mechanical stability of its surface when it is subjected to a NaOH treatment and a subsequent heat treatment to form an amorphous sodium titanate layer on its surface. Thus treated titanium metal is believed to be useful as a bone substitute even under highly loaded conditions.

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