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Formation of bioactive functionally graded structure on Ti-6Al-4V alloy by chemical surface treatment

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An Al- and V-free sodium titanate hydrogel layer with a graded structure where the sodium titanate gradually decreases toward the interior, was formed on the surface of Ti-6Al-4V alloy, when the alloy was exposed to 5 M NaOH solution at 60 °C for 24 h. This gel layer was transformed into an amorphous sodium titanate layer without giving considerable change in the graded structure, except a little increase in the depth of the oxygen distribution by a heat treatment at 600 °C for 1 h. The sodium titanate layer formed Ti-OH groups on its surface by exchanging its Na^+ ion with H_3O^+ ion in simulated body fluid when soaked in the fluid, and thus formed Ti-OH groups induced the apatite nucleation. The apatite layer also formed a graded structure toward the substrate. The strong bond of the apatite layer to the substrate was attributed to this graded structure.

1. Introduction

The present authors recently showed that bioactivity can be induced directly on pure titanium metal by subjecting the metal to a simple chemical surface treatment, i.e. NaOH and subsequent heat treatments [1–4]. A bioactive metal of this type is believed to be very useful as load-bearing bone substitutes, since it shows not only an intrinsic high fracture toughness but also a bone bonding ability. The titanium metal forms an amorphous sodium titanate layer on its surface by the NaOH and heat treatments. Thus formed sodium titanate layer forms Ti-OH groups on its surface by exchanging its Na^+ ion with H_3O^+ ion in the fluid in the body, to induce the apatite nucleation. Consequently, the titanium metal bonds to living bone through the apatite layer [5]. Since the sodium titanate is formed chemically *in situ* on the metal, it is integrated with the metal substrate by a graded structure without a distinct interface [6]. Therefore, the apatite layer formed on the metal also has a graded structure toward the substrate. Consequently, the apatite layer is strongly bonded to the substrate [7].

Titanium alloys were also shown to form the sodium titanate layer on their surfaces by similar NaOH and heat treatments [2]. This result may be important practically, since titanium alloys, more popularly Ti-6Al-4V, are being actually used as orthopaedic implants, because of their strengths and machinabilities superior to pure titanium metal. It is, however, not clear yet how alloying species such as Al and V affect the formation of sodium titanate by the NaOH and heat treatments and ultimately the formation of apatite on its surface in body environment. In the present study, surface structural changes of Ti-6Al-4V alloy with the NaOH treatments and subsequent exposure to simulated body fluid were investigated with a special interest on the effect of the alloying species.

2. Materials and methods

2.1. Specimen preparation

Ti-6Al-4V alloy (Kobe Steel Ltd, Japan), composition of which is given in Table I, substrates $10 \times 10 \times 1\ \text{mm}^3$ in size, whose surfaces were abraded with No. 400 diamond plate, were soaked in 5 ml of 5.0 M 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. The substrates were subsequently heated up to 600 °C at a rate of 5 °C/min, kept for 1 h and allowed to be cooled to room temperature in Ni-Cr electrical furnace.

The alloy substrates subjected to the NaOH and heat treatments were soaked in 24 ml of an acellular simulated

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TABLE I Contents of the Ti, Al and V in Ti-6Al-4V alloy and their amounts released into 5.0 M NaOH aqueous solution at 60 °C for 24 h

	Content* in the alloy/wt %	Released amount/μgcm^{-1} (Ratio %)
Ti	89.13	5.02 (41.56)
Al	6.45	4.96 (41.06)
V	4.16	2.01 (17.38)
Others‡	0.26	No detection (0)

*Data from Kobe Steel Ltd, Kobe 651, Japan.

‡Minor components such as Fe, C, N, O and H.

body fluid (SBF) [8] 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 for various periods. The SBF was prepared by dissolving reagent grade chemicals of 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. After given soaking periods, the substrates were removed from the SBF, washed with acetone, and dried in a clean bench.

2.2. Analyses of specimen surfaces and SBF

Surfaces of the Ti-6Al-4V alloy substrates before and after the NaOH and heat treatments and after 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 Auger electron spectroscopy (AES; Model MT4300, ULVAC-PHI Co., Japan). The AES measurements was performed at an Auger electron take-off-angle of 45° with Ar ion sputtering at a rate of 25 nm/min.

Element concentrations and pH of the SBF before and after soaking of the substrates were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP; Model SPS1500, Seiko Inst. Co., Japan) and an electrolyte-type pH meter (Model D-14, Horiba Co., Japan).

3. Results

Figs 1 and 2 show the SEM photographs and TF-XRD patterns of the surfaces of Ti-6Al-4V alloy substrates before and after 5.0 M NaOH treatment at 60 °C for 24 h and subsequent heat treatment at 600 °C for 1 h. A porous network structure was formed on the alloy substrate by the NaOH treatment. Broad peaks appeared at 23–29° and 48° on the XRD pattern after the NaOH treatment indicates that this porous layer is a hydrogel [3]. The hydrogel layer was fairly densified and small XRD peaks ascribed to crystalline sodium titanate ($Na_2Ti_5P_{11}$) and rutile (TiO_2) appeared after the subsequent heat treatments. This indicates that a sodium titanate hydrogel layer was formed by the former NaOH treatment and converted into dehydrated amorphous sodium titanate layer containing small amounts of the crystalline phases by the subsequent heat treatment.

Fig. 3 shows the AES depth profiles of the surfaces of Ti-6Al-4V alloy substrates before and after the NaOH treatment and subsequent heat treatment. The depth profile before treatment (A) shows that the surface of untreated alloy is covered with passive layer of titanium oxide about 1000 Å thick. After the NaOH treatment (B), new compositional gradients, where Na and O concentrations gradually decrease and Ti concentration gradually increases as a function of the depth up to about 4500 Å, appeared near the surface. This indicates that sodium titanate hydrogel layer formed on the alloy substrate by the NaOH treatment gradually decreases its content toward the substrate. Alloying species of Al and V were not detected up to a depth about 2000 Å, where the Na and O concentrations abruptly decreased. After the heat treatment (C), the distribution of the O extended to a depth about 10 000 Å while that of Na was almost unchanged. These changes are due to the conversion of the hydrogel into an amorphous sodium titanate and formation of a titanium oxide between the sodium titanate and the alloy substrate. The distributions of the

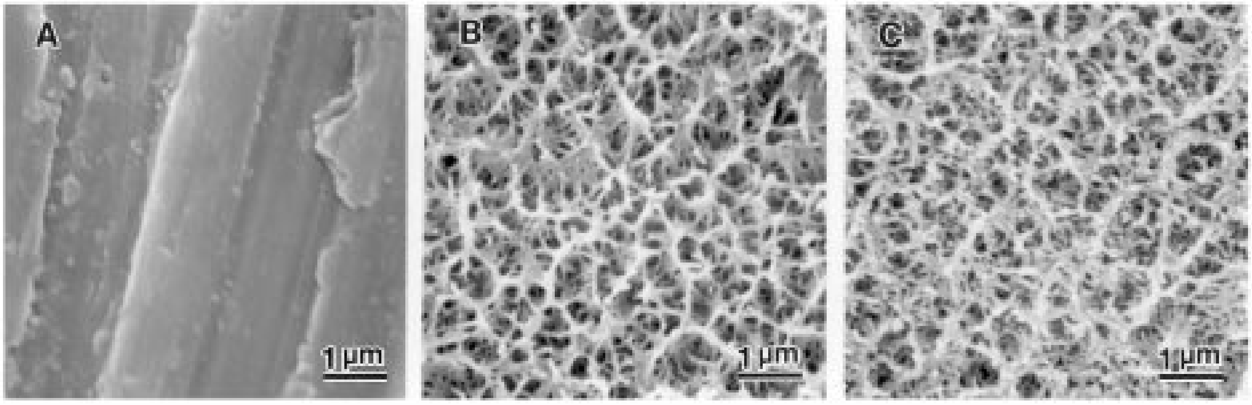

Figure 1 SEM photographs of the surfaces of Ti-6Al-4V alloy substrates before (A) and after (B) 5.0 M NaOH treatment at 60 °C for 24 h and (C) subsequent heat treatment at 600 °C for 1 h.

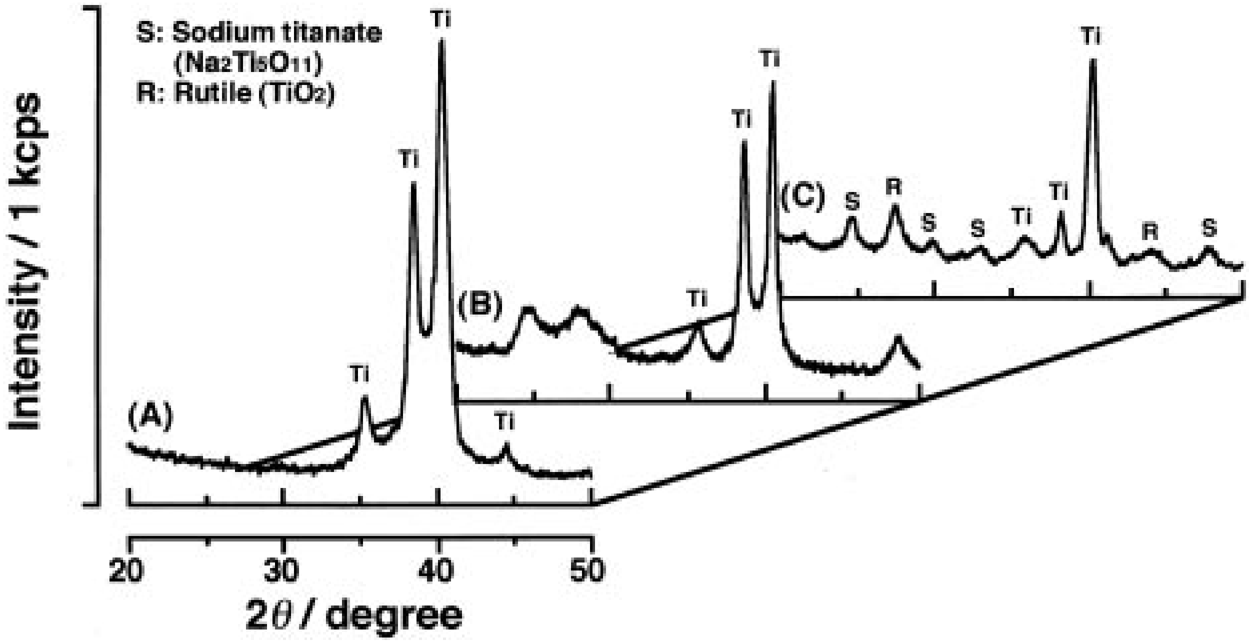

Figure 2 TF-XRD patterns of the surfaces of Ti-6Al-4V alloy substrates before (A) and after (B) 5.0 M NaOH treatment at 60 °C for 24 h and (C) subsequent heat treatment at 600 °C for 1 h.

Al and V moved inside the substrate to be detected from a depth about 4500 Å after the heat treatment. This is a depth where the distribution of the Na became negligible.

Table I shows the amounts of the Ti, Al and V released from the Ti-6Al-4V alloy into 5.0 M NaOH aqueous solution at 60 °C for 24 h. The alloying species of the Al and V occupied the amount as high as 58.44% of the released metallic elements. In view of their original contents in the alloy, this value is very high. This indicates that the Al and V are selectively released from the alloy during the NaOH treatment.

Figs 4 and 5 show the SEM photographs and TF-XRD patterns of the surfaces of Ti-6Al-4V alloy substrates soaked in SBF for various periods after 5.0 M NaOH treatment at 60 °C for 24 h and heat treatment at 600 °C for 1 h. Particle-like substances were observed to be formed on the alloy substrate after soaking for 5 days (B). They were ascribed to assemblies of tiny apatite crystals, since the XRD peaks newly appeared after this soaking period were all identified as those of crystalline apatite (B). The apatite grew to cover the whole surface of the substrate with increasing soaking time to 7 days (C). Apparent induction period of apatite formation on this alloy, i.e. 5 days, was a little longer than that of pure titanium metal subjected to the same NaOH and heat treatments, i.e. 3 days.

Fig. 6 shows changes in pH and element concentrations of SBF with soaking of Ti-6Al-4V alloy substrate subjected to the NaOH and subsequent heat treatments. The first event in SBF after soaking the alloy substrate was simultaneous and rapid increases in Na concentration and pH up to 3 days. This indicates that the alloy releases Na^+ ion from the surface sodium titanate via ion exchange with H_3O^+ in SBF soon after the soaking. No Ti as well as Al and V were detected to be released into SBF. Gradual decreases in Ca and P concentrations for a long soaking period are due to the apatite formation and

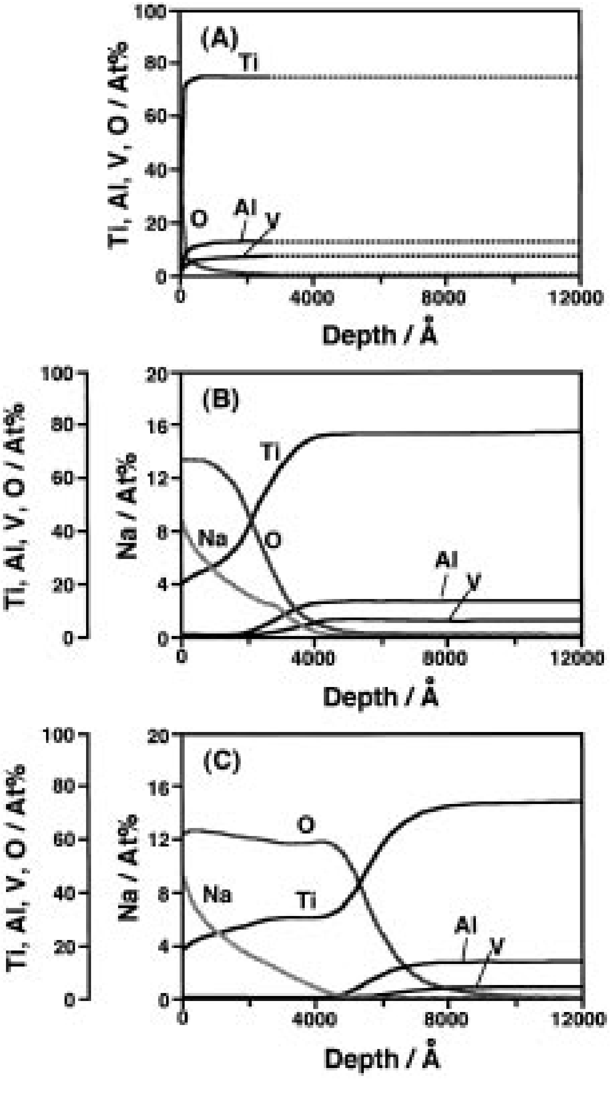

Figure 3 AES depth profiles of the surfaces of Ti-6Al-4V alloy substrates before (A) and after (B) 5.0 M NaOH treatment at 60 °C for 24 h and (C) subsequent heat treatment at 600 °C for 1 h.

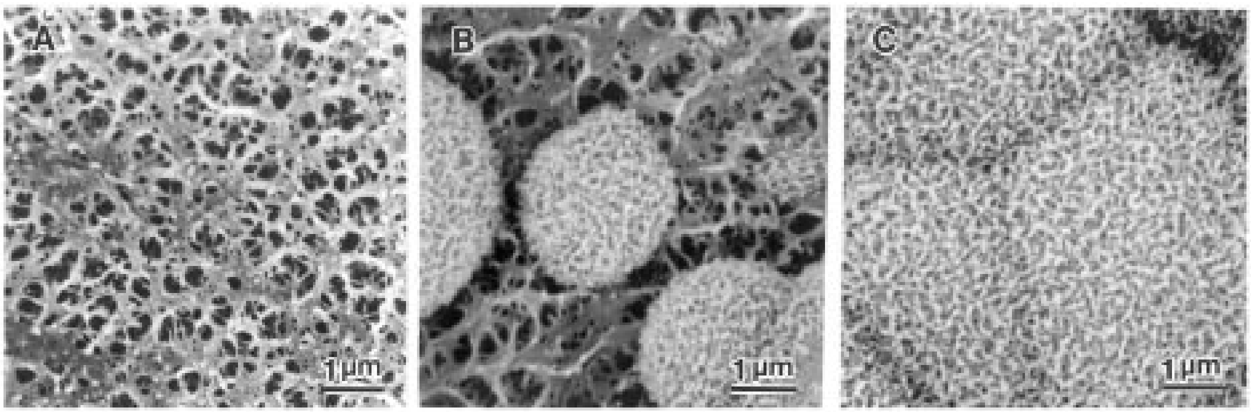

Figure 4 SEM photographs of the surfaces of Ti-6Al-4V alloy substrates soaked in SBF for (A) 3 days, (B) 5 days and (C) 7 days after 5.0 M NaOH treatment at 60 °C for 24 h and heat treatment at 600 °C for 1 h.

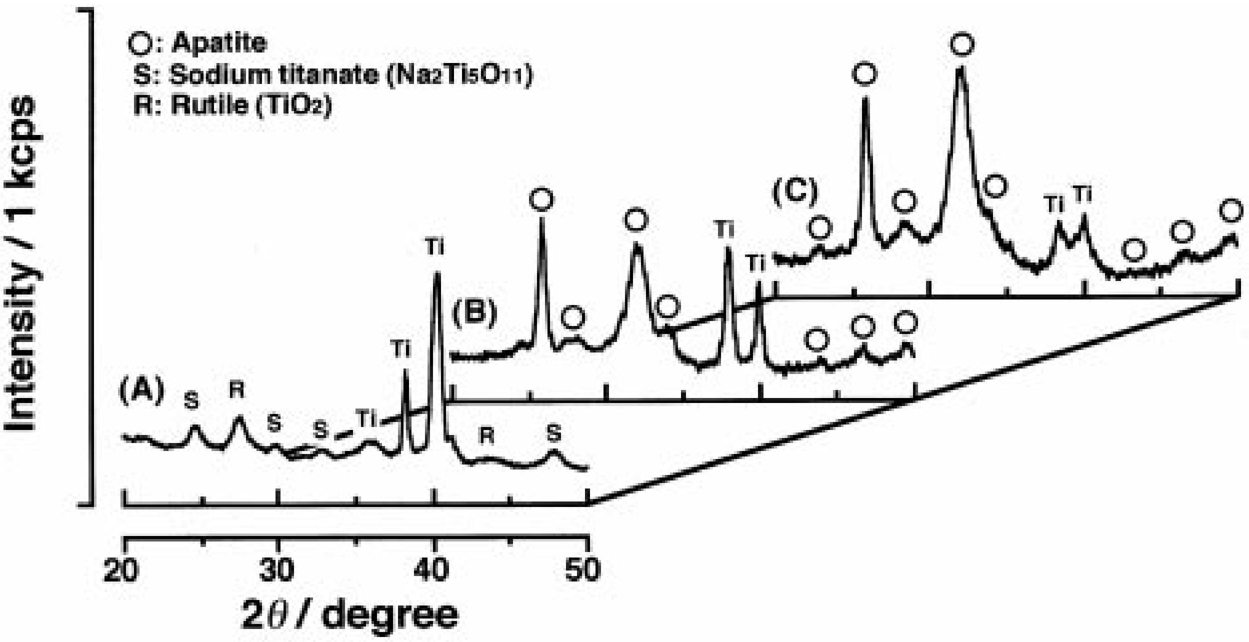

Figure 5 TF-XRD patterns of the surfaces of Ti-6Al-4V alloy substrates soaked in SBF for (A) 3 days, (B) 5 days and (C) 7 days after 5.0 M NaOH treatment at 60 °C for 24 h and heat treatment at 600 °C for 1 h.

growth on the alloy substrate which proceed by consuming them in SBF.

Fig. 7 shows AES depth profile of the surface of Ti-6Al-4V alloy substrate soaked in SBF for 5 days after the NaOH and subsequent heat treatments. The gradient of Na concentration present up to a depth of about 4500 Å before soaking disappeared completely after the soaking in SBF. This indicates that the Na^+ ion in the sodium titanate was all released into SBF. New compositional gradients, where the Ca and P concentrations gradually decrease up to the same depth appeared due to the apatite formation on the alloy substrate after soaking in SBF. The gradients of O, Ti, Al and V were almost unchanged even after the soaking in SBF.

4. Discussion

It is apparent from the above results that the NaOH and heat treatments provide a graded surface structure of an Al- and V-free amorphous sodium titanate even on Ti-6Al-4V alloy as on pure titanium metal. Being subjected to the NaOH treatment, the Ti-6Al-4V alloy releases selectively the Al and V to form a sodium titanate hydrogel layer on its surface (Figs 1–3, and Table I). The hydrogel layer is dehydrated and densified to be stabilized into an amorphous sodium titanate by the subsequent heat treatment (Figs 1–3). The amorphous sodium titanate is integrated *in situ* on the top surface of alloy by a graded structure, where the sodium titanate gradually changes into the alloy substrate through titanium oxide (Fig. 3). Alloying species of the Al and V do not exist in the sodium titanate in the graded structure, since they are not diffused from the interior to the surface during the heat treatment.

The apatite formation on the alloy in SBF could therefore be explained by the same mechanism as pure titanium metal. When the alloy substrate is exposed to SBF, the surface sodium titanate releases Na^+ ion via ion exchange with H_3O^+ ion in the surrounding SBF. The ion exchange forms a hydrated titania abundant in Ti-OH groups and increases the pH of SBF to increase the ionic activity product of apatite in the fluid. The Ti-OH groups

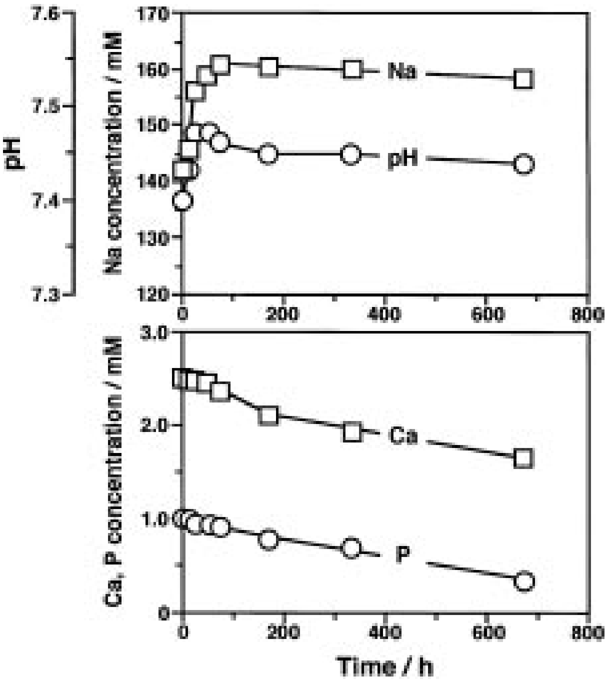

Figure 6 Changes in pH and element concentrations of SBF with soaking of Ti-6Al-4V alloy substrate subjected to 5.0 M NaOH treatment at 60 °C for 24 h and heat treatment at 600 °C for 1 h.

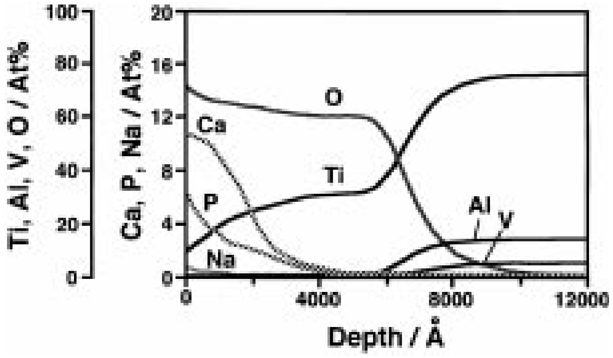

Figure 7 AES depth profile of the surface of Ti-6Al-4V alloy substrate soaked in SBF for 5 days after 5.0 M NaOH treatment at 60 °C for 24 h and heat treatment at 600 °C for 1 h.

of the hydrated titania induce the apatite nucleation on its surface, while the increased ionic activity product accelerates the apatite nucleation [9, 10]. As a consequence, a large number of apatite nuclei are formed on the surface of the alloy. Thus formed apatite nuclei spontaneously grow into a dense and homogeneous layer by consuming calcium and phosphate ions from the surrounding fluid (see Fig. 6). As a result, the graded surface structure of sodium titanate changes into one where the apatite on the top surface gradually changes into alloy substrate through hydrated titania and titanium oxide. This graded structure provides a strong bonding between the apatite and the alloy substrate [7]. It is already shown that the alloy tightly bond to and integrate with living bone through the apatite layer [11]. This tight bond is attributed to the graded structure revealed in the present paper.

5. Conclusions

The NaOH and heat treatments provide a bioactive graded surface structure on Ti-6Al-4V alloy, where an Al- and V- free amorphous sodium titanate on top surface gradually changes into the alloy substrate through titanium oxide. The sodium titanate transforms into a hydrated titania via Na^+ ion release to induce a bonelike apatite formation on the alloy substrate in body environment. In this process, the graded surface structure develops into one where the apatite on the top surface gradually changes into alloy substrate through hydrated titania and titanium oxide. This graded structure provides a strong interfacial bonding between the apatite layer and the alloy substrate, eventually a tight bonding of the alloy to living bone through the apatite layer.

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References

1. T. KOKUBO, F. MIYAJI, H. -M. KIM and T. NAKAMURA, *J. Am. Ceram. Soc.* **79** (1996) 1127.
2. H. -M. KIM, F. MIYAJI, T. KOKUBO and T. NAKAMURA, *J. Biomed. Mater. Res.* **32** (1996) 409.
3. *Idem.*, *J. Ceram. Soc. Japan* **105** (1997) 111.
4. *Idem.*, *J. Mater. Sci.: Mater. Med.* **37** (1997) 341.
5. W.-Q. YAN, T. NAKAMURA, M. KOBAYASHI, H.-M. KIM, F. MIYAJI and T. KOKUBO, *J. Biomed. Mater. Res.* **37** (1997) 265.
6. H.-M. KIM, F. MIYAJI, T. KOKUBO, S. NISHIGUCHI and T. NAKAMURA, *ibid.* in press.
7. H.-M. KIM, F. MIYAJI, T. KOKUBO and T. NAKAMURA, *J. Biomed. Mater. Res.: Appl. Biomater.* **38** (1997) 121.
8. T. KOKUBO, H. KUSHITANI, S. SAKKA, T. KITSUGI and T. YAMAMURO, *J. Biomed. Mater. Res.* **24** (1990) 721.
9. P. LI, C. OHTSUKI, T. KOKUBO, K. NAKANISHI, N. SOGA, T. NAKAMURA, T. YAMAMURO and K. DE GROOT, *ibid.* **28** (1994) 7.
10. T. KOKUBO, *Anales de Quimíca* **93** (1997) S49.
11. S. NISHIGUCHI, T. NAKAMURA, H. FUJITA, H. KATO, H.-M. KIM, F. MIYAJI and T. KOKUBO, in ''Bioceramics Vol. 11'', edited by R. Z. LeGeros and J. P. LeGeros (World Sci., Singapore, 1998) p. 675.

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