Potassium Titanate Nanorod Arrays Grown on Titanium Substrates and Their in vitro Bioactivity

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金属チタン上に成長したチタン酸カリウムナノロッド配列とin vitro 生体活性

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A novel approach to fabricating highly-oriented, nm-scale potassium titanate K$_2$Ti$_6$O$_13$ rod arrays on titanium substrates was demonstrated. The fabrication process was template-free, and simply involved coating the titanium substrates with pulverized potassium metaborate and its derivatives, and subsequent heating at 700°C for 5 h. When the samples were soaked in hot water, the coating layers were readily removed, leaving an array of titanate crystallites on the titanium substrates. Even the slightest change in the composition of the potassium borates resulted in various microstructures, while K$_2$O·1.03B$_2$O$_3$ yielded highly-oriented nanorod arrays of K$_2$Ti$_6$O$_13$. Bioactivity of the as-prepared nanorod arrays was proved by the deposition of apatite in simulated body fluid (SBF: Kokubo solution). When soaked in SBF, the K$_2$Ti$_6$O$_13$ nanorod arrays deposited apatite within one day accompanying the release of potassium ions from the crystallites into SBF and the arrays were covered with apatite layers in three days. Ion exchange between the potassium ions in the crystal and calcium ions in SBF is proposed as the mechanism operative to favor the deposition of apatite.

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1. Introduction

Two-dimensional nanorod array structures in the form of rods, tubes and others have attracted much attention for their potential applications.1–4 Several highly-oriented nanorod or nanotube arrays of, e.g., ZnO5–8 or TiO$_2$5–11 have so far been developed but the techniques may have disadvantages with respect to large-scale and low-cost fabrication, or application to complicated-shaped substrates, so, simpler and more convenient methods are demanded.

K$_2$Ti$_6$O$_13$ is semi-conductive and known for its catalytic capability.22 It belongs to the family of alkali titanates, about which ion-exchange reactions have been widely investigated.13 Since borates are good solvents for TiO$_2$, K$_2$Ti$_6$O$_13$ will be precipitated from a TiO$_2$-containing potassium borate flux, though Berkes et al.14 grew rutile using a sodium borate as the flux. In this case, solubility curves of TiO$_2$ in the flux or phase diagrams for the relevant systems are important. Anikin et al.15 examined the solubility of TiO$_2$ in potassium borates. Eastal and Udycz16 reported a partial phase diagram for K$_2$Ti$_6$O$_13$–K$_2$O·2B$_2$O$_3$, in which the solidus line horizontally lay at ~680°C and the liquid range extended above 800°C. After the phase diagram of the system K$_2$O–B$_2$O$_3$,77 K$_2$O·B$_2$O$_3$ (potassium metaborate) melts at 950°C while the solidus line that extends in the B$_2$O$_3$-rich region is in 787°C. Thus, when K$_2$O·B$_2$O$_3$ is in contact with a titanium substrate in air at a temperature of 700°C–750°C, titanium oxide will be derived from the oxidation of titanium and react with metaborate to yield potassium titanates. What is more, potassium metaborate is moderately hygroscopic and is easily dissolved in aqueous systems, hence only those titanates will be left on the titanium substrate.

The present paper demonstrates a novel and simple approach to fabricating nm-sized rod arrays of a potassium titanate, K$_2$Ti$_6$O$_13$, on metallic titanium substrates. In this method, pulverized potassium metaborate and its derivatives are coated on titanium substrates, heated, and subsequently removed in distilled water. It is expected that well-oriented nanorod arrays of K$_2$Ti$_6$O$_13$ develop on the titanium surface. This method is versatile and simple, thus avoiding expensive chemicals or special apparatus and involves no steps with complicated treatments.

In this experiment, attention has also been paid to examining the in vitro bioactivity of the K$_2$Ti$_6$O$_13$ nanorod arrays because Kim et al.19 reported that sodium titanate, Na$_2$Ti$_2$O$_5$, exhibited in vitro bioactivity. Here, bioactivity denotes a property of materials by which they spontaneously deposit apatite in a body environment. It has been established that such bioactive materials also deposit apatite in an aqueous solution or simulated body fluid (commonly denoted as SBF) of the Kokubo recipe. SBF contains the same inorganic ions as human blood plasma in similar concentrations.19 If they are bioactive, the present novel structure of potassium titanate promises potential applications to Ti-based biomedical implants and devices as well.

2. Experimental

Potassium metaborate and three derivatives with small variations were prepared. Table 1 lists the compositions of the borates, denoted as KB1, KB2, KB3 and KB4, where KB2 is the exact metaborate KBO$_2$ or K$_2$O·B$_2$O$_3$. The relevant titanium samples for which the coating layer was applied and removed are denoted as Ti-KB1, etc. Reagent grade potassium carbonate and boron oxide (Nacalai Tesque Inc.) were used as the starting materials. The batches were placed in a platinum crucible with a cover and melted in an electric furnace at 1200°C for 30 min. The melts were then quenched on a steel
plate. Since those potassium borates were out of the glass-forming region, the quenched products were partly devitrified. The obtained potassium borates were pulverized to powders with sizes of 30–100 μm, which were kept in a desiccator until use.

A sheet of 0.1-mm thick pure titanium (α-Ti; Nilaco) was cut into pieces of Ti substrates 10 × 10 × 0.1 mm in size. An approximately 1-mm thick layer of each potassium borate powder was applied directly onto the Ti substrates without forming a slurry. Then, the samples were heated up to 700°C at a rate of 10°C/min in an electric muffle furnace and maintained for 5 h. They were allowed to cool down to room temperature by cutting off the furnace power, then soaked in distilled water at 80°C for 5 h to remove the coating layers. After cleaning ultrasonically with distilled water the samples were stored in the desiccator before use in subsequent experiments.

The Ti–KB3 samples were selected to examine their in vitro bioactivity or ability to deposit apatite in SBF since they had well-ordered array structures. They were soaked in 10 ml of SBF and maintained at 36.5°C for 1, 2, 3, or 4 days. The pH value of SBF was measured at 36.5°C, and ion concentrations were measured by inductively coupled plasma atomic emission spectroscopy (ICP–AES, SPSS7700, Seiko Instruments).

The surface morphology of the samples was observed under a scanning electron microscope (JEOL JSM–6300) after coating a 30-nm gold layer, operated under 20 kV acceleration voltage and 300 mA emission current. The crystal phases that appeared on the titanium substrates were identified by an X-ray diffractometer (CuKα, RINT 2500, Rigaku) with a thin-film attachment, operated under 40 kV acceleration and 200 mA current, and 2θ scanning mode with incident angle of 1° at a scanning rate of 3°/min. Differential thermal analysis (DTA) was measured by a thermal analysis system (TAS-300, Rigaku) in the temperature range of 25–1000°C at a heating rate of 10°C/min. The DTA technique was also applied to examine the reaction between Ti and the potassium borates. The as-received Ti powder (Furuuchi Chem. Corp.) with a purity of 99.9% (passed through a 300-mesh grid) was mixed with the borate powders at a weight ratio of 1:2. DTA traces were obtained in the temperature range of 25–1000°C at a heating rate of 10°C/min. The mixtures with KB1 and KB2 gave very similar DTA traces, hence the DTA results were described for those with KB1, KB3, and KB4.

3. Results
3.1 Reactions between Ti and potassium borate powders
All of the quenched KB powders consisted mainly of KBO₂ according to their XRD identification patterns (not shown here). The powders were reacted with the titanium substrate when heated together. The heating mixtures of the KB powders and titanium powder may simulate those reactions.

Table 1. Batch Composition of Potassium Borate Powders used for Coating on the Titanium Substrates

<table>
<thead>
<tr>
<th>Sample</th>
<th>K₂O mol</th>
<th>B₂O₃ mol</th>
<th>Morphology of K₂Ti₆O₁₆ crystals</th>
<th>Size</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>KB1</td>
<td>1.05</td>
<td>1.00</td>
<td>μm-scale rods</td>
<td>random</td>
<td></td>
</tr>
<tr>
<td>KB2</td>
<td>1.00</td>
<td>1.00</td>
<td>μm-scale rods</td>
<td>random</td>
<td></td>
</tr>
<tr>
<td>KB3</td>
<td>1.00</td>
<td>1.03</td>
<td>μm-scale rods</td>
<td>purer</td>
<td></td>
</tr>
<tr>
<td>KB4</td>
<td>1.00</td>
<td>1.05</td>
<td>μm-scale rods</td>
<td>random</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 shows TG–DTA traces for their powder mixtures. All traces involved a smaller endothermic bending at 650°C and a broad exothermic peak in the range of 700° to 800°C. Possible exothermic reactions are the formation of titanium oxide, rutile or anatase, and some potassium titanates. In order to identify the phases that appeared in the mixtures, a preliminary XRD analysis was conducted for the KB–titanium mixtures after heating at 700°C up to 5 h. It was found for all of the KB–titanium mixtures that
1) K₂Ti₆O₁₆ and KTiO₅ evolved concurrently but no titanium oxide was detected within 3 h,
2) after heating for 5 h, KTiO₅ disappeared, and both rutile and K₂Ti₆O₁₆ were present in the borate matrix.

It follows that KTiO₅ is metastable and was transformed to K₂Ti₆O₁₆ by extracting potassium oxide out of the metastable matrix. When the mixtures were heated at 800°C for 1 h, they gave XRD patterns characteristic of amorphous materials in addition to those for rutile, K₂Ti₆O₁₆ and titanium. In addition, the TG traces displayed large weight gains in the range of 700–800°C. Therefore, the large exothermic peak together with sharper ones in the DTA traces in Fig. 1 were contributed by not only precipitation of the potassium titanates and their dissolution into the borate matrix to form a vitreous matrix but also vigorous oxidation of titanium. The titanium mixtures with KB1 and KB3 displayed a discernable endothermic bending around 650°C in the DTA traces, while the KB4 mixture had an exothermic hump at around the 650°C range. The profiles around the bending were very similar to the profile characteristics of glass transition. Since such DTA profiles were not observed for sole potassium borate powders, some reactions took place between the KB and titanium powders. From those preceding experiments, it was concluded that since 700°C was high enough for titanate precipitation reactions but adequately low for preventing too much oxidation of titanium, it was selected as the coating temperature.

3.2 K₂Ti₆O₁₆ growth on titanium substrates
Figure 2 shows the surface morphology of the titanate crystals derived from titanium substrates due to heating with the KB powders at 700°C for 5 h. The morphology depended greatly on the composition of the KB powders. Sample Ti–KB1, derived from powder KB1 with a slightly larger K₂O/ B₂O₃ ratio (1.05/1.00), yielded randomly grown, μm-scale
and Ti-KB2 derived from the KB powders having the ratio K₂O:B₂O₃ ≥ 1 consisted primarily of K₂Ti₅O₁₃ with a small fraction of anatase (JCPDS #21-1272) and some unknown phases. This indicates the μm-scale crystallites that covered the surface of Ti-KB1 and Ti-KB2 are K₂Ti₅O₁₃. As can be seen in Fig. 3, Ti-KB3 yielded rutile as its major phase, and its X-ray diffraction intensity even exceeded that of K₂Ti₅O₁₃ in Ti-KB4. Note here that the profiles for Ti-KB1 and Ti-KB2 were significantly different from those for Ti-KB3 and Ti-KB4 in the diffraction of K₂Ti₅O₁₃ in the range of 2θ > 25°. The latter two had many weaker diffractions of K₂Ti₅O₁₃ above 30° in addition to those of (110), (310) and (31-1) at 24.1°, 29.2° and 29.8°, respectively. In contrast, the former two only showed the (110) diffraction without any weaker diffractions of K₂Ti₅O₁₃ above 25°. That is, on samples Ti-KB1 and Ti-KB2 the potassium titanate rods preferably exposed (110) planes that were roughly parallel to the titanium substrate surface, taking into account the 2θ scanning mode of TF-XRD measurement. The K₂Ti₅O₁₃ rods for Ti-KB3 show a moderate degree of preferred growth since the (110) diffraction was much stronger than the (310) and (31-1) ones. In the case of Ti-KB4, the diffractions in the range of 2θ > 25° are significantly stronger and comparable to those for, e.g., (310), which indicates that the rods arranged randomly on the substrate exposing their various planes parallel to the substrate surface.

3.3 Influence of the heating time

After heat treatment for 5 h, nanorod arrays evolved on titanium in the case of Ti-KB3, whereas not on other samples. Figure 4 illustrates this morphological evolution dependent on the heating time. When the KB3 powder was spread out and a titanium substrate was maintained for 1 h at 700°C, a layer of discrete and μm-size orthorhombic ribbon-like crystals covered the substrate surface. From the XRD diffraction pattern in Fig. 5 (1 h), the rods were primarily comprised of K₂Ti₅O₁₃ accompanied by a small fraction of anatase. After 3 h (Fig. 4 (b)), many nm-sized, thin, wiry rods ~0.1 μm in width appeared and, what is more, they grew on the previously grown thicker ribbon-like rods, resulting in a “two-story” structure. When the sample was maintained at 700°C for 5 h (Fig. 4 (c)), the thinner rods grew to cover the whole surface, while the ribbon-like crystallites could not be observed under SEM. Those nm-scale rods grew in length to several μm, while...
they maintained their original width of about 100 nm to form highly upward-oriented arrays, as displayed in Figs. 4(c) and (d). In addition, the rods displayed a marked mono-dispersion in terms of width and length.

TF-XRD patterns in Fig. 5 display the changes in crystalline phases as the heating time increased from 1 to 5 h. In 1 h, $\text{K}_2\text{Ti}_6\text{O}_{13}$ appeared with a trace of anatase and a smaller fraction of unidentifiable phases that gave a group of peaks ranging from 27° to 30°. Within 3 h, the peaks in that range were separated, and the peak at 27.5° was identified to be the (110) diffraction of rutile. Although the 25.3° peak of anatase grew in 3 h to indicate an increase in the fraction of anatase, it disappeared after the KB3-coated Ti substrates were heated for 5 h. At the same time, the group of peaks ranging around 28° were finally separated into the diffractions of rutile and $\text{K}_2\text{Ti}_6\text{O}_{13}$. In spite of the growth of rutile, $\text{K}_2\text{Ti}_6\text{O}_{13}$ was the primary phase for the 5-h sample, in which the crystallites preferred aligned exposing (110) planes roughly parallel with the substrate surface.

It is interesting to note that the morphology of samples Ti-KB1 and Ti-KB2 in Fig. 2 (heated with the powders for 5 h) is the same as that of sample Ti-KB3 in Fig. 4(a) (heated for 1 h). This implies that the morphology in Figs. 2(a) and (b) is that of the earlier stage to the formation of the nanorod array for sample Ti-KB3. In other words, it is suggested that the nanorods are produced even on Ti-KB1 and Ti-KB2 after much longer heating.

3.4 In vitro apatite deposition

Figures 6 and 7 show the TF-XRD patterns and SEM images for titanium sample Ti-KB3 after soaking in SBF up to 4 d. The other samples gave similar results. Within 2 d in SBF, the XRD patterns were the same as those for the as-prepared sample, without showing any diffractions of apatite (JCPDS 9-0432) that are supposed to appear at 25.9° and 31.8°. Nevertheless, Fig. 7(a) shows that tiny spherical crystallites of about 3 μm in diameter are scattered on the surface, and Fig. 7(b) shows that their number and size increased after being soaked for 3 d. The XRD profile in Fig. 6: 3d exhibits the apatite diffractions at 25.9° and 31.8°. Thus, those spherical particles observed in Fig. 7(a) are apatite. The particles in Fig. 7(b) are about 5 μm in diameter, sitting on top of the array. Some neighboring particles are joined together, giving a cocoon-like shape, and some grew across the rods at their middle parts or tips. Figure 7(c) indicates that apatite covered the whole surface when the sample was soaked for 4 d in SBF.

Figure 8 plots the ion concentrations of Ca(II), P(V), K(I) and B (III) in SBF as a function of the soaking time. The concentration of B (III) was below the detection limit of the ICP apparatus, that is, the borate residues were practically absent in the rod-forming samples. The concentrations of both Ca (II) and P (V) decrease steadily with increasing the soaking time in accordance with the apatite deposition, demonstrated in Figs. 6 and 7. In contrast, the concentration of K(I) increased progressively. Those potassium ions were not from the borate coating but from $\text{K}_2\text{Ti}_6\text{O}_{13}$, because no residues of the KB particles remained on the sample surface as no B (III) was detected in Fig. 8. The release of K(I) from $\text{K}_2\text{Ti}_6\text{O}_{13}$ caused no apparent changes in the XRD profile in Fig. 6, which can be interpreted as showing that the lattice degradation is restricted only in the top surface of the rods and only a little, if any. The pH remained almost constant at 7.40-7.35 throughout the soaking period (up to 4 d), as illustrated by the solid line in Fig. 9.
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4. Discussion

4.1 Nanorod array growth

After Ankin et al.\textsuperscript{15} the solubility of TiO\textsubscript{2} in potassium borate melts decreases drastically as the B\textsubscript{2}O\textsubscript{3} fraction increases, e.g., 25\% in K\textsubscript{2}B\textsubscript{4}O\textsubscript{7}, 0.01\% in KB\textsubscript{2}O\textsubscript{4} and 0\% in B\textsubscript{2}O\textsubscript{3} (by weight; at 900°C). In the present case, the KB powders would not melt at the heating temperature of 700°C since the solubility for the potassium metaborate-diborate range is at 787°C.\textsuperscript{17} Yet, heating not only the Ti and KB powder mixtures but also the titanium substrates with the KB powders yielded K\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5}. A preliminary experiment indicated that oxidation of pristine titanium substrates is vigorous only above 800°C, whereas titanium powder was susceptible to stimulated oxidation above 750°C. That is, the heating at 700°C gave only a small amount of titanium oxide at the surface of titanium particles and the substrate. The oxide reacted with the KB powders due to some solid-state reaction mechanism, taking advantage of greater solubility. The chemical state of Ti(IV) in the KB matrix is not clear. Still, K\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} was precipitated accordingly when the amount of Ti(IV) exceeded the solubility limit in the KB matrix. This obviously accompanies the formation of a matrix richer in B\textsubscript{2}O\textsubscript{3}. Those series of change in the borate matrix cause diverse effects regarding the dissolution of titanium oxide and precipitation of K\textsubscript{2}Ti\textsubscript{4}O\textsubscript{13}.

Extraction of K\textsubscript{2}O out of K\textsubscript{2}O·B\textsubscript{2}O\textsubscript{3} theoretically yields K\textsubscript{2}O·2B\textsubscript{2}O\textsubscript{3} in the vicinity of the crystallites. When the system is in equilibrium, it leaves a mixture of K\textsubscript{2}O·B\textsubscript{2}O\textsubscript{3} and K\textsubscript{2}O·2B\textsubscript{2}O\textsubscript{3} with a eutectic (787°C) at ~60 mol\% in the K\textsubscript{2}O content. In the present case, the changes occur in a non-equilibrium manner, hence it is highly possible that an amorphous moiety is produced. K\textsubscript{2}O·2B\textsubscript{2}O\textsubscript{3} melts at 815°C\textsuperscript{17} and is in the largest K\textsubscript{2}O content limit of the glass-forming composition range. Sakka and Mackenzie\textsuperscript{20} listed 403°C for its glass transition temperature (\(T_g\)), confirming an empirical rule of \(T_g = 2/3 \ T_m\) melting point; \(T_f\) temperature of liquidus; \(T_g\) and \(T_m\) are 7, and the amorphous matrix around the first precipitates would melt, resulting in glass. Diffusion through glass is much more favored than that through crystalline matrices. In addition, it is commonly accepted that diffusion through a grain boundary in sintered ceramics is much faster than bulk diffusion. In the first stage of potassium titanate precipitation, a multiphase structure will appear: TiO\textsubscript{2} layer on Ti/K\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5}/glass with Ti(IV)/KB, where/\textquoteleft denotes a boundary. Once such glass is formed, it is likely that Ti(IV) diffuses from the titanium oxide layer into the glass/KB boundary because this boundary region is richer in K(1) and TiO\textsubscript{2} is more soluble there than in the titanate crystal/glass boundary. K(1) is supplied from the bulk KB particle to the growing crystallite across the glass phase. Therefore, concentration gradients of K(1) and Ti(IV) are established across the glass phase. When potassium titanate embryos form on the titanium oxide or titanate crystals that were formed by oxidation of the substrate, they then start growing linearly by virtue of the concentration gradient.

It is worthwhile to mention that topotaxial effect possibly operates at the beginning stage of potassium titanate growth. Based on the crystallographic analysis, titanium atoms in K\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} (010) plane and α-Ti (002) plane have similar arrangement, though in the former case large interstitial positions present among the Ti sub-lattices. When K\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} is derived from titanium, the atomic arrangement in the hexatitanate would reflect that in the Ti metal. Such topotaxial effect was already reported in the growth of rutile rod arrays on titanium substrate by Liu et al.\textsuperscript{21} And also, Wang et al.\textsuperscript{22} and Wu et al.\textsuperscript{23} employed such topotaxial effect to explain how hydrated rutile and anatase favor precipitation of hydroxyapatite in SBF.

4.2 Rods growth direction

K\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} crystal belongs to monoclinic system and its b-axis inclines 90° to α–c planes and prefers to develop fibrous shapes with b-axis parallel with the fiber axis at the high degree of undercooling, i.e., difference between growth temperature and melting point (1370±15°C).\textsuperscript{24} Such growth was commonly reported in several literatures.\textsuperscript{25,26} In the present experiment, K\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} rods grew up at 700°C which is 670°C lower than its melting point, thus it is reasonable to propose that these fibrous K\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} rods have grown up along its b-axis, i.e., [010] direction, although (110) plane gave the strongest diffraction. Noted that such discrepancy was ever observed in the case of rutile rod arrays grown through a similar glass phase topotaxial (GPT) nucleation.\textsuperscript{21}

The growth along b-axis will lead to the K\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} rods bearing perpendicularly on their ends. However, in the case of Ti-KB3 the nm-sized rods actually grow up on a layer of discrete, μm-sized K\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} crystals which give a rough topography, as displayed in Fig. 4(a), it is an adverse for all the rods to align in the direction perpendicular to the substrate.
surface. As a result, the arrays varied their orientation to some degree. This was supported by the fact that TF-XRD analysis conducted under \( (\theta-2\theta) \) scanning mode (not shown) gave a similar profile to that under 26 scanning mode. For example, X-ray diffraction intensity ratios of \((110)/(310)\) of the \( K_2TiO_3 \) phase on Ti-KB3 were 2.40 in \( (\theta-2\theta) \) scanning mode and 2.47 in 26 scanning mode \((\theta=1)\) in contrast to 0.67 of JCPDS Card. This indicates that the growth direction of the arrays was considerably limited by the rough substrate topography though the growth of \( K_2TiO_3 \) rods was highly preferred in [010] direction.

4.3 Effects of the composition of the KB powders

Because of only a slight difference in composition, a preliminary study with NMR and XRD techniques showed, accordingly, that these potassium borate powders had practically the same structure. Yet, one should find some reasons or factors for the fact that the \( K_2TiO_3 \) rods grown on the titanium substrates have different morphologies depending on the composition of the borates. When the ratio \( K/B < 1/1, \) nm-size \( K_2TiO_3 \) rods were obtained, growing in a preferred orientation as in the case of Ti-KB3 and Ti-KB4 but in diverse orientations. In contrast, with the ratio \( K/B \geq 1/1, \) \( \mu m \)-size \( K_2TiO_3 \) rods grew along the substrate surface. Note that in the case of Ti-KB3, such \( \mu m \)-size crystals were formed within 1 h but the nm-size rods were only observed after heating for 5 h. At this moment, no solid explanation is available, but at least that which should be emphasized is the importance of the solubility of titanium oxide and potassium titanate in the KB flux or the molety derived from them in the course of precipitation. The 5-h heating for Ti-KB1 and Ti-KB2 (in Fig. 2) and the 1-h heating for Ti-KB3 (Fig. 4(a)) led to a similar structure. This implies that the surface morphology in Fig. 4(a) is established for Ti-KB3 in the relatively earlier stage of heating, while nanorod arrays might be formed in the former two after longer heating if the titanium substrates could stand it. With Ti-KB4, however, \( K_2TiO_3 \) nanorods evolved within 30 min, suggesting that a different reaction route might be operated.

4.4 Apatite deposition

The release of potassium ions into SBF from the potassium titanates will increase the pH if the resulting Ti-O bonds are hydrolyzed in SBF. Actually, the pH increased, as the \( K_2TiO_3 \)-neutrophilic titanium substrates were soaked in SBF. The hydrolysis reaction is:

\[
> Ti-O-K + H_2O \rightarrow > Ti-OH + K^+ + OH^- \quad (1)
\]

Knowing the concentration of potassium ions in Fig. 8, Eq. (1) derives by calculation that the pH of SBF should increase as illustrated by the dashed line in Fig. 9. However, contrary to the calculation, the pH of SBF decreased slightly as displayed by the solid line in Fig. 9. The decrease in pH is supposed to be due only to the formation of apatite, which consumed the \( OH^- \) groups out of SBF.

\[
10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 \quad (2)
\]

Assuming deposition of such stoichiometric hydroxyapatite on the titanium substrates, the measured calcium ion concentration gives pH, which is plotted by the dotted line in Fig. 9 and agrees with the experimental results.

Since the members in the alkali titanate family \( A_2TiO_{2n+1} \) \((1 \leq n \leq 8)\) are capable of ion exchange in an aqueous solution, \(^{13}\) it is highly probable that ion exchange takes place among the potassium ions of the titanate and the calcium ions in SBF:

\[
2Ti-O \cdot K + Ca^{2+} \rightarrow (Ti-O_1/2)_2 \cdot Ca + 2K^+ \quad (3)
\]

Equation (3) interprets well the changes in Fig. 8: the concentration of \( K(1)^+ \) (= [K(1)]) increased and that of \( Ca(II)^+ \) (= [Ca(II)]) decreased within 1 d. In this earlier stage, apatite formation (Eq. (2)) could not interpret the decrease in [Ca(II)] because there was no accompanying decrease in the concentration of P(V). Equation (3) postulates that both the decrease in [Ca(II)] and increase in [K(1)] are 1: 2 in a molar ratio. Figure 8 indicates that the increment in [K(1)] was about 0.2 mM after Ti-KB3 was soaked in SBF for 1 d. Then, the decrease in [Ca(II)] should be 0.1 mM, assuming that Eq. (2) is the only mechanism to describe the ion concentration change. In fact, the initial decrease in [Ca(II)] within 1 d was about 0.08 mM. It follows that, at the earlier stage, the K-Ca ion exchange at the interface of the SBF-\( K_2TiO_3 \) rods mostly contributes to the change in [K(1)] and [Ca(II)].

From the viewpoint of ion activity product (IAP), \(^{27}\) the potassium ions released from the rod array to SBF affect the thermodynamic stability of SBF regarding apatite deposition when they are involved in the apatite lattice. It is natural and commonly accepted by Ohtsuki et al. \(^{27}\) and Tsuru et al. \(^{28}\) that an increase in the component ions of apatite, such as calcium and hydroxyl ions, in SBF favors deposition of apatite when an equilibrium is established among those ions. This is accounted for in terms of IAP:

\[
IAP = \Pi \quad (activity \ of \ the \ apatite \ component \ ions \ in \ SBF)
\]

In the present case, potassium ions were not incorporated in the apatite lattice as proven by EDX. Thus, the K(1) concentration itself has nothing to do with the SBF stability although Kim et al.\(^{19}\) suggested that sodium and potassium ions released from glasses in the system \( M_2O-TiO_2-SiO_2 \) \((M=Na, \ K)\) accelerate apatite nucleation. One possible effect is to increase the pH (or hydroxyl ion concentration) by Eq. (1), where the hydroxyl ion is one of the components of apatite. Kim et al.\(^{29}\) explained the induction of apatite deposition by NaOH-treated titanium using such an increase in the pH. However, the pH of SBF was almost constant in this experiment, even decreasing slightly, as mentioned above. Therefore, the most plausible explanation of the deposition of apatite on the of \( K_2TiO_3 \) rods is that local calcium ion content near the rod surface is increased due to the ion exchange among the calcium ions in SBF and the potassium ions in the rod lattice. The ion exchange is most likely to take place on the rod tip, and the accumulated Ca\(^{2+}\) ions would attract hydroxyl and phosphate ions. In fact, it has been found in Fig. 6(a) that apatite is deposited on the upper part of the nanorod arrays, instead of growing in the inter-rod space near the roots of the rod arrays.

5. Conclusion

Potassium titanate \( K_2TiO_3 \) in the form of nanorod arrays was fabricated on a titanium substrate through a simple interface reaction between potassium borate coatings and metallic titanium. The array structures were significantly dependent on the compositions of potassium borates and the heat treatment time. Highly-oriented nanorod arrays of \( K_2TiO_3 \) were obtained when potassium borate \( K_2O-1.03B_2O_3 \) was applied and the heating time was maintained up to 5 h at 700°C. The rod arrays seemingly grew on the surfaces of the \( \mu m \)-scale \( K_2TiO_3 \) crystalite layer that grew on the substrate in the beginning step. Bioactivity of the as-achieved nanorod arrays
was proved by the deposition of apatite in SBF within 3 d, attributing to the local accumulation of calcium ions near the rod surface due to the ion exchange between the calcium ions in SBF and the potassium ions in the rod lattice.

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