

# Development of hafnium metal and titanium-hafnium alloys having apatite-forming ability by chemical surface modification

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journal or publication title	Journal of biomedical materials research. Part B, Applied biomaterials
volume	106
number	7
page range	2519-2523
year	2017-12-23
その他のタイトル	Development of bone-bonding hafnium metal and titanium-hafnium alloys by chemical surface modification
URL	<a href="http://hdl.handle.net/10228/00007021">http://hdl.handle.net/10228/00007021</a>

doi: <https://doi.org/10.1002/jbm.b.34068>



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Journal:	<i>Journal of Biomedical Materials Research: Part B - Applied Biomaterials</i>
Manuscript ID	JBMR-B-17-0566.R2
Wiley - Manuscript type:	Original Research Report
Date Submitted by the Author:	n/a
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Keywords:	Hafnium, Titanium-hafnium alloy, Bone-bonding, Surface treatment, Apatite

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6 **Development of hafnium metal and titanium-hafnium alloys having**  
7 **apatite-forming ability by chemical surface modification**  
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**Abstract**

Hafnium (Hf) has attracted considerable attention as a component of biomedical titanium (Ti) alloys with low Young's moduli and/or shape-memory functionalities, because its cytotoxicity is as low as that of Ti. The drawback of metals is that their bone-bonding ability is generally low. It is known that apatite formation in the body is a prerequisite for bone-bonding. Although several chemical treatments have been proposed for preparing Ti for bone-bonding, there have been no similar investigations for Hf. In the present study, NaOH- and heat-treatments were applied to pure Hf and Ti-Hf alloys and their bone-bonding ability was assessed *in vitro* with the use of simulated body fluid (SBF). After NaOH- and heat-treatments, anatase formed on alloys with low Hf content (20–40% (atom%) Hf); mixtures of sodium titanate and hafnium titanate formed on alloys with similar Ti and Hf content (60% Hf); and hafnium oxide formed on alloys with high Hf content (80% Hf and pure Hf). Precipitates of apatite were observed on all the metals in SBF, except for the alloy with 60% Hf. We speculated that the hafnium titanate formed on this alloy had a low apatite-forming ability owing to its high negative surface charge, which inhibited P adsorption. The apatite-forming abilities of the Ti-Hf alloys strongly

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6 depended on their Hf content. The present results indicate that Hf-based materials have  
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9 good potential for bone-bonding.  
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15 **Keywords:** Hafnium, Titanium-hafnium alloy, Bone-bonding, Surface treatment,  
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18 Apatite  
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## 1. Introduction

Hafnium (Hf) belongs to the same group of elements as titanium (Ti) and zirconium (Zr), which are applied for clinical replacement of hard tissue and have similar chemical properties. It is known that the cytotoxicity of hafnium is as low as that of Ti and Zr [1]. Recently, addition of Hf to Ti has been found to reduce the Young's modulus of the resulting alloy from 120 to 110 GPa [2,3]. In addition, Hf has attracted considerable attention as a component of nickel-free shape memory alloys for medical applications [4].

However, many metallic materials do not bond with bone easily and this property must be improved to enable their application to hard tissue reconstruction. An essential requirement for artificial materials to exhibit bone-bonding in the body is the formation of a bone-like apatite layer [5]. Chemical treatments based on aqueous solutions of sodium hydroxide (NaOH) [6] or hydrogen peroxide [7], followed by heat treatments, and anodic oxidation [8] are known to be effective techniques for enhancing the apatite-forming ability on Ti metal surfaces. Tantalum (Ta) [9] and Zr [10] can also exhibit bone-bonding properties following NaOH treatments. However, the effects of such surface treatments on Hf remain unclear.

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6 In this study, pure Hf metal and Ti-Hf alloys were subjected to NaOH- and  
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9 heat-treatments and the apatite-forming abilities of the treated alloys were investigated in  
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12 simulated body fluid (SBF). Differences in the apatite-forming ability are discussed in  
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15 terms of the components of the alloy and the crystalline phase of the surface after the  
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18 treatments.  
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## 20 21 22 23 24 **2. Materials and methods**

### 25 26 27 **2.1. Materials**

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30 NaOH and the reagents used to prepare SBF were purchased from Nacalai Tesque  
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33 Inc., Kyoto, Japan, hafnium oxide (HfO<sub>2</sub>) from Kojundo Chemical Laboratory Co., Ltd.  
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36 Saitama, Japan, and anatase from Ishihara Sangyo Kaisha, Ltd., Osaka, Japan.  
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### 40 41 42 **2.2. NaOH- and heat-treatments**

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46 Pure Hf substrates (Nilaco Co., Tokyo, Japan) 10 × 10 × 0.1 mm<sup>3</sup> in size and Ti-Hf  
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49 alloy substrates (Kindly prepared by arc melting in Institute for Materials Research,  
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52 Tohoku University, Sendai, Japan) 5 × 5 × 7 mm<sup>3</sup> in size were polished with #500 SiC  
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6 paper. Ti-Hf alloy containing x atom% of Hf is hereafter denoted as Ti-xHf. Each  
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9 substrate was then soaked in 5 mL of 10 M-NaOH aqueous solution and mechanically  
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12 agitated in a water bath (H-10, Taitec Co., Saitama, Japan) at 60 °C for 1 day. The  
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15 agitating speed was fixed at 120 strokes/min. The substrates were then removed from  
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18 solution, gently washed with ultrapure water, and dried at 60°C. The substrates were  
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21 then heated to 400°C at 5 °C/min, maintained at 400°C for 1 h, and allowed to cool to  
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24 room temperature in the furnace.  
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28 Hafnium oxide and hafnium titanate (HfTiO<sub>4</sub>) powders were used for zeta potential  
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31 measurements as model compounds for the surface crystal phase of the chemically  
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34 treated metals. The HfO<sub>2</sub> reagent was used as received. HfTiO<sub>4</sub> was prepared by  
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37 calcinating a mixture of HfO<sub>2</sub> and anatase at a molar ratio of 1:1 at 1300°C for 5 h.  
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40 X-ray diffraction measurements confirmed that the obtained powder consisted of a  
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43 single phase of HfTiO<sub>4</sub> (JCPDS#40-794).  
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### 46 47 48 49 2.3. Soaking in SBF 50

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53 The treated substrates were soaked in 30 mL of SBF containing the following  
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6 inorganic ion concentrations (142.0 mM Na<sup>+</sup>, 5.0 mM K<sup>+</sup>, 1.5 mM Mg<sup>2+</sup>, 2.5 mM Ca<sup>2+</sup>,  
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9 147.8 mM Cl<sup>-</sup>, 4.2 mM HCO<sub>3</sub><sup>-</sup>, 1.0 mM HPO<sub>4</sub><sup>2-</sup>, and 0.5 mM SO<sub>4</sub><sup>2-</sup>) at 36.5 °C for  
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12 various periods. The pH of the solution was buffered at 7.40 by 50 mM  
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15 tris(hydroxymethyl)aminomethane and an appropriate amount of HCl. SBF was  
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18 prepared according to the literature [11]. After soaking, the substrates were removed  
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21 from the SBF and then immersed in ultrapure water for 30 min to remove excess  
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25 water-soluble salts on their surfaces.  
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#### 31 2.4. Characterization 32 33

34 The surface structural changes of the substrates were characterized by scanning  
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37 electron microscope imaging (SEM; Model S-3500N; Hitachi Co., Tokyo, Japan),  
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40 energy dispersive X-ray spectroscopy (EDX; Model EX-400; Horiba Co., Kyoto, Japan),  
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43 thin-film X-ray diffraction (TF-XRD; MXP3V; Mac Science Ltd., Yokohama, Japan),  
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46 X-ray photoelectron spectroscopy (XPS, KRATOS AXIS-Nova, Shimadzu Co., Kyoto,  
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49 Japan) and Fourier-transform infrared spectroscopy (FT-IR, FT/IR-6100, JASCO Co.,  
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52 Tokyo, Japan). Zeta potentials of the powder in 10 mM NaCl were measured with a  
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6 zeta-potential analyzer (ELS-Z, Otsuka Electronics Co., Osaka, Japan) in a connected  
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9 box-like quartz cell. The obtained zeta potential was statistically analyzed by t-test.  
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12 In TF-XRD experiments, the incident beam was fixed at  $1^\circ$  to the surface of each  
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14 substrate, at a scan rate of  $0.02^\circ \cdot \text{s}^{-1}$ . In XPS experiments, the measured binding energies  
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16 were corrected against the C1s binding energy of hydrocarbon methylene groups (284.6  
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18 eV) adsorbed on the substrate surface. In FT-IR measurements, an attenuated total  
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20 reflection (ATR) attachment with a diamond crystal was used.  
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### 31 **3. Results**

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34 Fig. 1 shows XPS spectra of NaOH- and heat-treated metal substrates. Peaks at 530 eV  
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36 are assigned to M-O (M: Ti, Hf), those at 531 eV to acidic M-OH or physically adsorbed  
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38 water, and those at 532.5 eV to basic M-OH or chemically adsorbed water [12]. The  
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40 proportion of the peak attributed to basic M-OH groups or chemically adsorbed water  
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42 increased as the Ti content in the alloy increased. This result indicates that the NaOH- and  
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44 heat-treatments induced the largest proportion of M-OH groups on the surface of the  
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46 alloys with high Ti content.  
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6 Fig. 2 shows TF-XRD patterns of the NaOH- and heat-treated metal substrates before  
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9 and after immersion in SBF for 7 days. Peaks assigned to the  $\alpha'$  phase of Ti-Hf with a  
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12 hexagonal close-packed structure shifted to a lower diffraction angle as the Hf content in  
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15 increased in the alloy. Peaks assigned to anatase (JCPDS#21-1272) were observed for  
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18 Ti-20Hf and Ti-40Hf; peaks assigned to  $\text{Na}_2\text{Ti}_5\text{O}_{11}$  (JCPDS#11-289) and  $\text{HfTiO}_4$   
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21 (JCPDS#40-794) were found in Ti-60Hf; peaks assigned to  $\text{HfO}_2$  (JCPDS#34-104) were  
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24 found in Ti-80Hf and Hf. Such crystalline phase was not observed except base metal just  
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27 after NaOH treatment (data not shown), meaning that the above oxides were formed by  
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30 the heating. The crystalline phases remained almost the same even after immersion in  
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33 SBF.  
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37 Fig. 3 shows SEM images and EDX spectra of the NaOH- and heat-treated metal  
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40 substrates after immersion in SBF for 7 days. Formation of spherical particles was  
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43 observed on the surfaces of the alloys except for the Ti-60Hf substrate. The particles were  
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46 confirmed to contain a high proportion of Ca and P by EDX.  
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50 Fig. 4 shows a high-magnification SEM image and FT-IR ATR spectrum of the  
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53 spherical particles formed on the surface-treated Ti-80Hf after immersion in SBF for 7  
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6 days. A fine network morphology was observed, which was similar to that of the  
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9 bone-like apatite formed in SBF [13]. In the FT-IR ATR spectrum, peaks assigned to  
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12  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$  and  $\text{CO}_3^{2-}$  were observed [14,15]. The peak of  $\text{HPO}_4^{2-}$  and  $\text{CO}_3^{2-}$  around  
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15  $870\text{ cm}^{-1}$  was too close to distinguish from each other. The splitting of the  $\text{PO}_4^{3-}$  peaks at  
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18  $600$  and  $1000\text{ cm}^{-1}$  is characteristic of apatite, and the presence of  $\text{CO}_3^{2-}$  suggested the  
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21 formation of carbonate-containing non-stoichiometric apatite in SBF [16]. Therefore, the  
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24 spherical particles in Fig. 3 are considered to be bone-like apatite.  
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28 Table 1 shows the zeta potentials of  $\text{HfO}_2$  and  $\text{HfTiO}_4$ , indicating that  $\text{HfTiO}_4$  had a  
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31 more negative surface charge than that of  $\text{HfO}_2$ .  
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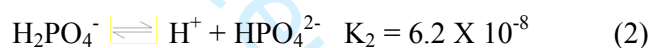
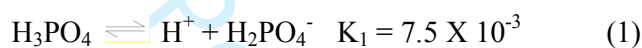
#### 33 34 35 36 37 **4. Discussion** 38

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40 We found that NaOH- and heat-treated Hf metal formed apatite on their surfaces in SBF.  
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43 This result confirms that the Hf-OH group can act as a functional group that enables  
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46 apatite formation, as previously reported for Si-OH and Ti-OH groups.  
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50 The calcium phosphate precipitates formed on the substrates could not be identified  
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53 as an apatite phase by TF-XRD, likely because of the small amount present. However, it  
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6 has been reported that pure Ti treated with 5 M-NaOH and heated at 400°C forms  
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9 apatite over its whole surface in SBF within 7 days [17]. Therefore, we observe that the  
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12 apatite-forming ability of the Ti-Hf alloy and Hf metal is lower than that of pure Ti.  
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15 There are two possible reasons for this result: First, the apatite-forming ability of  
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18 Hf-OH itself is lower than that of Ti-OH. Second, Ti has a higher corrosion rate (5.0  
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21 mm / year in 40% NaOH at 121°C) in NaOH solution than that of Hf (0.15 mm / year in  
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24 38% NaOH at 115°C) [18,19]. Therefore, it is likely that fewer Hf-OH groups were  
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27 formed by the NaOH- and heat-treatments, in spite that we used more concentrated  
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30 NaOH (10 M) than previous research on surface treatment of Ti (5 M) [17]. This  
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33 assumption is supported by our XPS spectra, which showed a low proportion of OH  
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36 groups on the treated metals with high Hf content in Fig. 1. It is reported that a lot of  
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39  $\text{Na}_2\text{Ti}_5\text{O}_{11}$  was mainly formed on Ti metal after 5 M-NaOH treatment and subsequent  
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42 heating at 600°C [17], while amount of  $\text{Na}_2\text{Ti}_5\text{O}_{11}$  formed on the treated Ti-Hf alloy was  
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45 very low (See Fig. 2). Therefore, this may also lead to low apatite formation on the  
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48 present specimens in SBF. Chemical treatment of Hf metal with a more concentrated  
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51 NaOH solution might be necessary in future studies.  
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6 It is noted that the formed apatite contained  $\text{HPO}_4^{2-}$  (See Fig. 4). Although Kokubo *et*  
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9 *al.* developed bone-bonding Ti by 5 M-NaOH treatment and subsequent heat treatment at  
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12 600°C, the apatite layer formed in SBF has not been characterized by FT-IR. On the other  
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15 hand, other groups have reported that  $\text{HPO}_4^{2-}$ -containing apatite is detected on Ti and its  
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18 alloys treated with 10 M-NaOH and heated at 600°C after soaking in SBF [20,21]. Acidic  
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21 dissociation of phosphoric acid is described as follows:  
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34 It is assumed that approximately 60% of phosphate species takes a form of  $\text{HPO}_4^{2-}$  at  
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37 pH7.40 based on these equilibria. Therefore, ion exchange would occur between  $\text{HPO}_4^{2-}$   
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40 in SBF and  $\text{CO}_3^{2-}$  in the apatite crystals which are equivalent anion.  
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44 Apatite was not formed on the Ti-60Hf, with an intermediate composition. The  
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47 proportion of OH groups on the surface of this substrate was similar to those of Ti-80Hf  
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50 and pure Hf, which both promoted apatite formation (See Fig. 1). Therefore, the low  
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53 proportion of OH groups was unlikely to be the reason for the lack of apatite formation.  
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6 Our zeta potential measurements indicated that the surface of HfTiO<sub>4</sub> was highly  
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9 negatively charged (see Table 1). The surface charge was much lower than that of Ti  
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12 metal subjected to the NaOH- and heat-treatments (approximately -10 mV), which  
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15 formed apatite [22]. Apatite nucleation on negatively charged materials such as NaOH-  
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18 and heat-treated Ti and Ta, and Na<sub>2</sub>O-SiO<sub>2</sub> glass is triggered by initial Ca<sup>2+</sup> adsorption  
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21 followed by PO<sub>4</sub><sup>3-</sup> adsorption [23,24,25]. Although Ca and P were detected on Ti-60Hf,  
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24 the amounts were smaller than those of the other samples (see Fig. 3). Hence, we  
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27 assume that the negative surface charge was neutralized by Ca<sup>2+</sup> adsorption onto HfTiO<sub>4</sub>  
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30 but further PO<sub>4</sub><sup>3-</sup> adsorption was limited.  
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## 5. Conclusion

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41 In this study, the apatite-forming abilities of pure Hf and Ti-Hf alloys subjected to  
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44 NaOH- and heat-treatments were investigated in SBF. The following points were  
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47 clarified.

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50 (1) Pure Hf metal subjected to the treatments enabled formation of apatite on its surfaces.

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53 Therefore, Hf is a candidate metallic material, which exhibits bone-bonding potential.  
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6 (2) The apatite-forming ability of Ti-Hf alloys was low at intermediate compositions.  
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9 Namely, apatite formation was not observed in Ti-60Hf. We speculate that highly  
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12 negatively charged  $\text{HfTiO}_4$  inhibited  $\text{PO}_4^{3-}$  adsorption.  
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### 18 **Acknowledgments**

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20  
21 The authors thank Ms. Akiko Nomura and Mr. Kazuo Obara of Institute for Materials  
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24 Research, Tohoku University, Sendai, Japan for their contribution to sample alloy  
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27 preparation.  
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Table 1 Zeta potentials of the samples (N=3)

Sample	Zeta potential (mV)
HfO <sub>2</sub>	-15.5±1.79
HfTiO <sub>4</sub>	-41.9±2.05*

\* $p < 0.001$  in comparison with HfO<sub>2</sub>

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6 **Figure captions**  
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8  
9 **Fig. 1** XPS spectra of NaOH- and heat-treated metal substrates. This shows that surface  
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12 OH content is different by composition of the alloy.  
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14  
15 **Fig. 2** TF-XRD patterns of NaOH- and heat-treated metal substrates before (left) and  
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18 after (right) immersion in SBF for 7 days. This shows that surface crystalline phase is  
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21 significantly different by composition of the alloy.  
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24 **Fig. 3** SEM images and EDX spectra of NaOH- and heat-treated metal substrates after  
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27 immersion in SBF for 7 days. Star marks indicate the positions of EDX analysis. Apatite  
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30 formation was not observed for intermediate composition of Ti-60Hf.  
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34 **Fig. 4** High-magnification SEM images and FT-IR ATR spectrum of the spherical  
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37 particles formed on the surface of the treated Ti-80Hf substrate after immersion in SBF  
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40 for 7 days. This shows that the formed apatite contains  $\text{HPO}_4^{2-}$  and  $\text{CO}_3^{2-}$ .  
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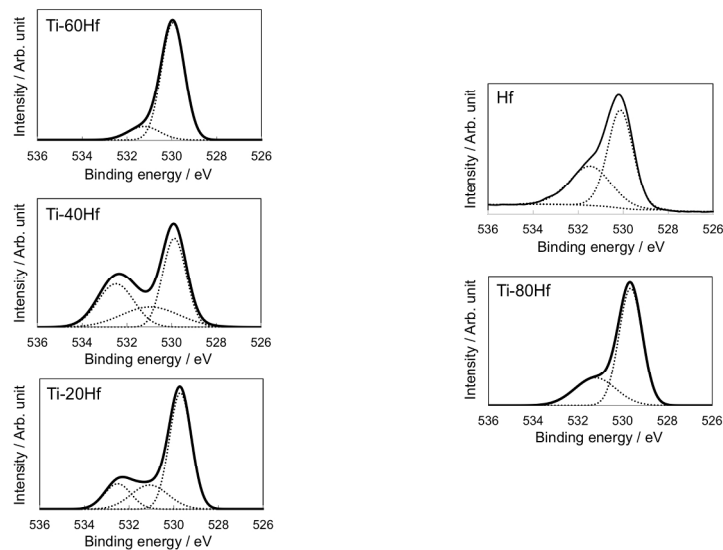


Fig. 1

Fig.1

338x190mm (180 x 180 DPI)

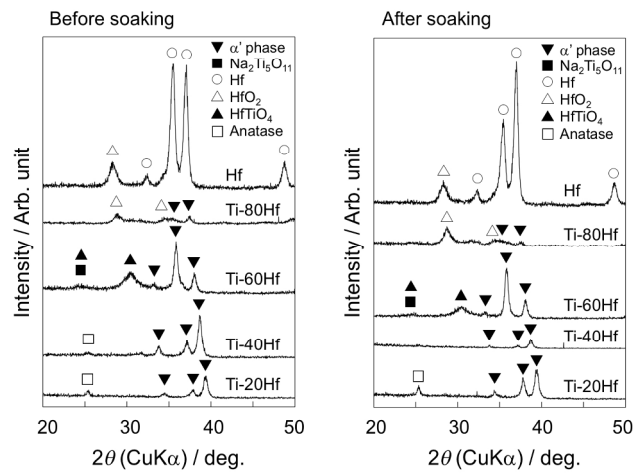


Fig. 2

Fig.2

338x190mm (180 x 180 DPI)



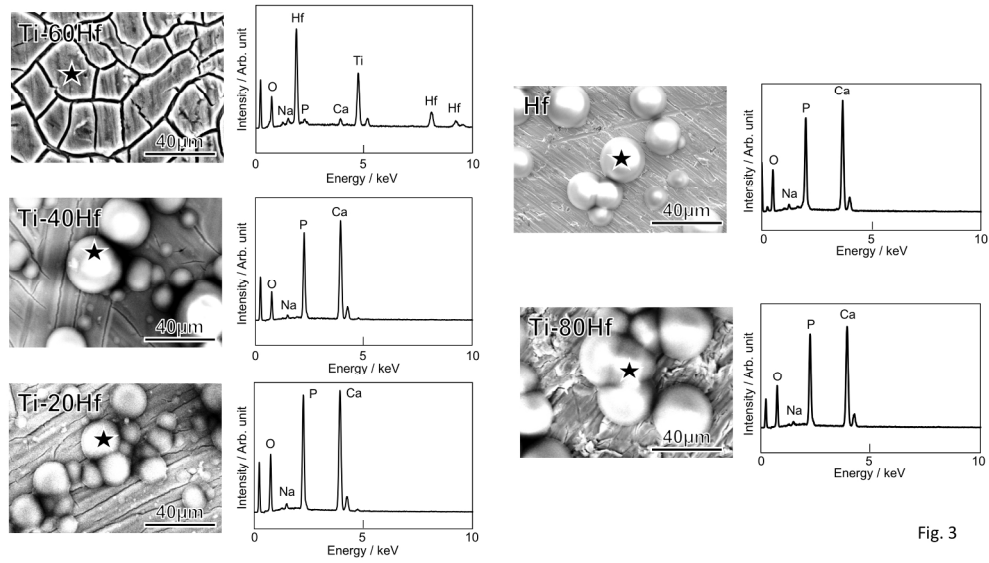


Fig. 3

Fig.3

338x190mm (180 x 180 DPI)

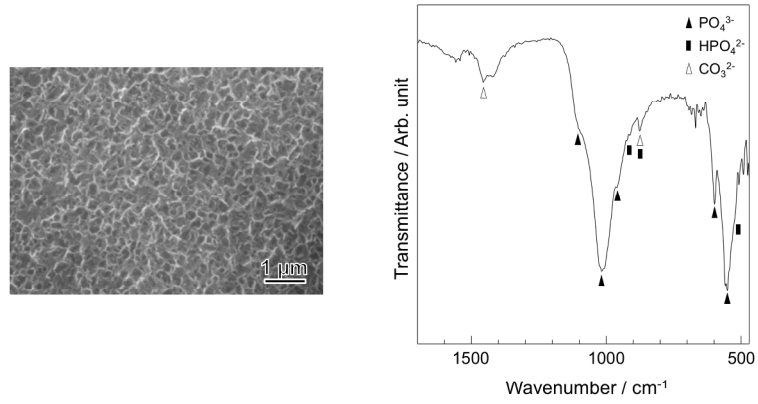


Fig. 4

Fig.4

338x190mm (180 x 180 DPI)