

# Functionally Gradient Bonelike Hydroxyapatite Coating on a Titanium Metal Substrate Created by a Discharging Method in HBSS Without Organic Molecules

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**Purpose:** This study evaluated the quality of coatings on titanium surfaces prepared by discharging in Hanks' balanced salt solution without organic molecules (HBSS<sup>-</sup>). **Materials and Methods:** 10×10×1.0-mm titanium plates were used as cathodes of a coating device developed in the laboratory and immersed in HBSS<sup>-</sup>. A piece of platinum foil was used as a counterelectrode. Discharging was maintained at 1 A and 10 V (416 mA/cm<sup>2</sup>) for periods of 90, 270, and 540 seconds. Crystal phases of the coatings were identified by x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). In addition, the surface characterization and Ca/P atomic ratio of the titanium surfaces were determined by x-ray photoelectron spectroscopy (XPS). Furthermore, the surface topography, the thickness of the coatings, and the bonds between coatings and titanium substrates were observed by scanning electron microscopy. **Results:** The FTIR and XRD studies demonstrated that the deposits on the titanium after 540 seconds of discharging were crystalline hydroxyapatite. In addition, the thickness of the titanium suboxide layer increased during discharging. The XPS studies indicated that after 540 seconds of processing, the mean Ca/P ratio of the coatings on the titanium was 1.71, which is similar to that of human bone. **Discussion:** In addition, the replacement of sodium ions with calcium ions seemed important for the promotion of crystallization of the coating. Furthermore, the XPS studies demonstrated that the coatings had a gradient function. Scanning electron microscopy showed that adhesion between coatings and the titanium substrate was close. The coatings were approximately 1 μm thick. **Conclusion:** These findings suggest that a very thin crystalline bonelike hydroxyapatite coating with a gradient function could be prepared on a titanium metal substrate in HBSS<sup>-</sup> by a discharging method. INT J ORAL MAXILLOFAC IMPLANTS 2004;19:177–183

**Key words:** hydroxyapatite, titanium

Hydroxyapatite (HA) coatings on metal implants have received much attention within dentistry because of their high rate of osteoconductivity and

promotion of early fixation to the bone around implants. However, since commercially available HA coatings are relatively thick (50 to 100 μm), they are easily damaged at the interface of the implant and the bone.<sup>1-3</sup> Detached coating particles are pathogens and can cause peri-implantitis.<sup>4</sup> Therefore, a technique for creating a thinner HA coating (< 1 μm) is desirable.

Conventional plasma spraying, flame spraying, and chemical techniques have all been investigated as techniques for producing a thinner HA coating on a metal substrate.<sup>5-7</sup> However, the bond formed between HA coatings and the metallic substrate by the spraying method, formed primarily through mechanical interlocking, is not strong enough. Additionally, the spraying method is unsatisfactory

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for applying a thinner, uniform HA coating on implants because of their complicated shapes. On the other hand, electrochemical methods, electrophoretic techniques in particular, seem attractive for forming HA coatings on titanium implants with complicated shapes. However, the bond between the coating and the metal substrate is significantly weak. In addition, because the deposits are not highly crystalline, and because a small electric field is created using this technique, additional secondary treatments (eg, hydrothermal treatment, heat densification) have been necessary to improve the quality of coatings.<sup>8,9</sup>

The authors hypothesized that a discharging technique in an electrolyte is useful for preparing thin calcium phosphate coatings on titanium surfaces.<sup>10</sup> Calcium phosphate (CaP) ions dissolved in an electrolyte were driven onto a titanium surface, where they formed a CaP layer stoichiometry with a larger electric field than that created by conventional electrophoretic techniques. This technique seemed promising for improving the quality of coatings without secondary treatments.

Initially, Fujimori and coworkers had difficulty preparing a thin layer of CaP deposits precipitated on titanium surfaces by discharging in an acidic-mixed CaP solution.<sup>11</sup> The deposits were porous and adhered weakly to titanium substrates. Subsequently, Kishida obtained strong adhesion between the coating and the titanium substrate using a 2-stage discharging method in an acidic-mixed CaP solution.<sup>12</sup> First, a titanium plate was anodic-oxidized in the solution. Subsequently, components of the solution were precipitated through a pretreated anodized layer by discharging with reversed polarity. The adhesion between the coating created and the titanium substrate was stronger than that shown in a previous study.<sup>11,12</sup> Nevertheless, because the coating was precipitated through the anodizing titanium dioxide (TiO<sub>2</sub>) layer, Kishida could not thin the coating to a thickness of 1  $\mu$ m. Furthermore, the coating included various calcium compounds (eg, calcium hydroxide) in addition to HA.

In the present study, a new method for preparing thin HA coatings on titanium surfaces was examined: discharging in Hanks' balanced salt solution without organic molecules (HBSS<sup>-</sup>) using an experimentally developed device rather than discharging in acidic-mixed CaP solution. Crystal phases of the coatings were identified by x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). In addition, the surface characterization and Ca/P atomic ratio of the titanium surfaces were determined by x-ray photoelectron spectroscopy (XPS). Furthermore, the surface topography, the

thickness of the coatings, and the bonds between the coatings and the titanium substrates were observed by scanning electron microscopy (SEM).

## MATERIALS AND METHODS

### Preparation of the Specimens and the Discharging Fluid

Japanese Industrial Standard grade 2 titanium plates (30×30×1.0 mm KS-50; Kobe Steel, Kobe, Japan) were used. They were divided into specimens of 10×10×1.0 mm using a wire-type electric discharge-machining device ( $\alpha$ -0iA; FANUC, Yamanashi, Japan). Subsequently, the specimens were gradually ground with waterproof polishing papers from #500 to #1200 (Sankyo, Rikagaku, Tokyo, Japan) under running water, and then polished with alumina particles (0.3  $\mu$ m average diameter). The prepared specimens were cleaned ultrasonically in acetone for 15 minutes, in a detergent solution (7;180; MP Biomedicals, Aurora, OH) for 15 minutes, and in distilled water for 15 minutes. They were then dried and stored for 24 hours at 23°C in a desiccator that maintained 50% humidity.

The electrolyte solution used in this study was Hanks' balanced salt solution without organic molecules (HBSS<sup>-</sup>), prepared in the laboratory with an ion concentration of 142.0 mmol/L Na<sup>+</sup>, 5.5 mmol/L K<sup>+</sup>, 8 mmol/L Mg<sup>2+</sup>, 1.26 mmol/L Ca<sup>2+</sup>, 140.0 mmol/L Cl<sup>-</sup>, 8.25 mmol/L HPO<sub>4</sub><sup>2-</sup>, and 4.2 mmol/L HCO<sub>3</sub><sup>-</sup>, buffered at 7.4 pH with adequate hydrochloric acid. The HBSS<sup>-</sup> was stored in a polypropylene bottle for 1 day at room temperature before the following studies were undertaken.

### Discharging Protocol

The specimen was used as a cathode for the coating device and immersed in HBSS<sup>-</sup>. A 5×10×0.1-mm platinum plate was used as a counterelectrode. Discharging was generated by increasing cathodic potential beside working electrodes in the solutions and between the electrolyte and the working electrode through a gas layer on the surface of the electrode. Discharging was maintained at 1 A and 10 V (416 mA/cm<sup>2</sup>) for periods of 90, 270, and 540 seconds. Afterward, specimens were washed in distilled water and stored in a desiccator for 24 hours at 23°C in 50% humidity.

### Crystal Phases

Each coating was ground into particles and prepared as potassium bromide (KBr) pellets that were analyzed by an FTIR system (WS/IR-7300, JUSCO, Tokyo, Japan) with a spectra resolution of 4 cm<sup>-1</sup> to

characterize the various functional groups on the coating surface.

The crystal phases of each specimen were identified by XRD (XRD-6100, Shimadzu, Kyoto, Japan) with CuK $\alpha$  radiation. The XRD machine was operated at 40 kV (40 mA) with a scanning speed of 0.005 deg/s and a scanning range of 20 to 50 degrees ( $\Theta = 0.5$  degrees).

### Surface Characterization

The surface of each specimen was analyzed by XPS (ESCA-3400, Shimadzu). High resolution spectra of the Ti2p, O1s, C1s, Na1s, P2p, Ca2p, Cl2p, and K2p were analyzed using Mg K $\alpha$  radiation. A 20-mA emission current and an accelerated voltage of 8 kV were used for this analysis. After the initial XPS analyses, specimens were sputtered by an ion gun for 100 seconds and analyzed again by XPS. The binding energies of each spectrum were calibrated using a C1s spectra of 285.0 eV.

### SEM Observation

The specimens were prepared by gold vaporizing with a vacuum evaporation device (IB-2, Eiko Engineering, Ibaraki, Japan). The surface topography of the specimens was observed using a scanning electron microscope (S-2360N; Hitachi, Tokyo, Japan). They were sectioned with a low-speed saw (Isomet; Buehler, Lake Bluff, IL) and observed by SEM to evaluate the thickness of the coatings.

The Ca/P ratio of each coating was calculated using the relative concentrations of calcium and phosphorus. Results of the tests were expressed as the mean  $\pm$  standard deviation (SD) of 6 specimens. The findings were studied statistically using an analysis of variance (ANOVA). Significant differences were considered to exist when  $P < .01$ .

## RESULTS

### Crystal Phases

Figure 1 shows the FTIR spectra of specimens. The PO $_4^{3-}$  absorption peaks around 1,000 cm $^{-1}$  and 600 cm $^{-1}$  were clearly observed after the 90- and 270-second treatments, but the HA spectra were not. The CO $_3^{2-}$  absorption peaks around 1,500 cm $^{-1}$  and 860 cm $^{-1}$  were observed on each specimen. The PO $_4^{3-}$  absorption peaks around 1,000 cm $^{-1}$ , 600 cm $^{-1}$ , and 580 cm $^{-1}$  were observed after 540 seconds of treatment. In addition, since the peak of 3,570 cm $^{-1}$  attributed to hydroxide (OH $^-$ ) groups was observed after 540 seconds, the coating on the surface could be identified as HA. These spectra were similar to those of mineral-phase bone. Because the

PO $_4^{3-}$  peaks of the coatings were split around 600 and 580 cm $^{-1}$ , their crystallinity was relatively high.<sup>13</sup>

The XRD patterns of the specimens are shown in Fig 2. The HA pattern was clearly detected on the specimen processed for 540 seconds. Since no specific pattern was detected on the specimens with shorter processing times, the coatings of the specimens processed for 90 and 270 seconds were low in crystallinity. The peaks of titanium suboxide (TiO) became clear with a longer processing time.

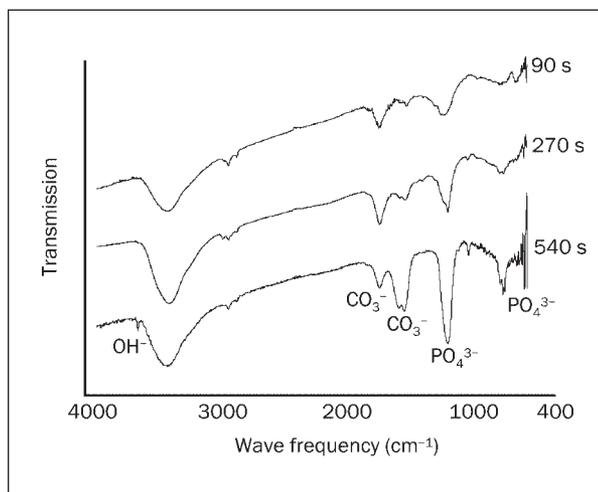
### Surface Characterization

The mean Ca/P ratio of each specimen was 1.54 (90 seconds) to 1.71 (540 seconds). The mean Ca/P ratio of the coatings created in 540 seconds coincided with that of bone ( $1.71 \pm 0.01$ ).<sup>14</sup>

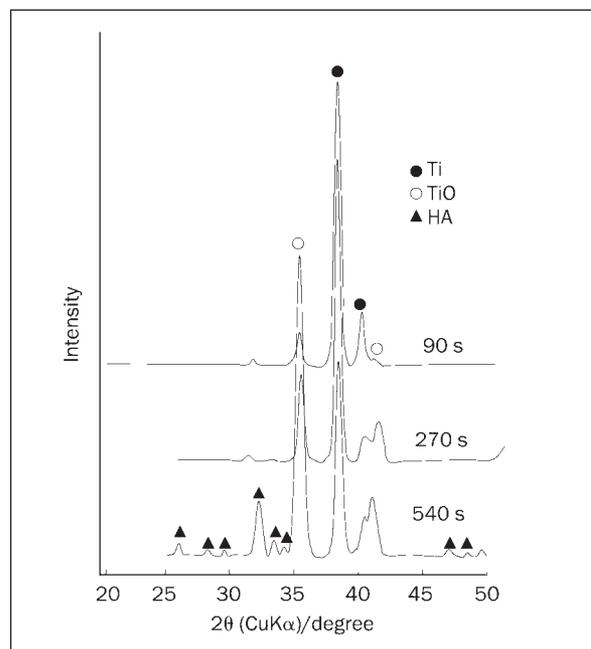
Since the relative concentration of titanium ( $3.35\% \pm 0.04\%$  after 90 seconds,  $2.54\% \pm 0.02\%$  after 270 seconds, and  $0.67\% \pm 0.02\%$  after 540 seconds) decreased with a longer discharging time (Fig 3a), and the relative concentrations of calcium ( $8.02\% \pm 0.02\%$  after 90 seconds,  $9.14\% \pm 0.04\%$  after 270 seconds, and  $10.92\% \pm 0.01\%$  after 540 seconds) and phosphorus ( $5.2\% \pm 0.02\%$  after 90 seconds,  $5.86\% \pm 0.01\%$  after 270 seconds, and  $6.36\% \pm 0.01\%$  after 540 seconds) increased with a longer discharging time ( $P < .01$ ), the densities of calcium and phosphorus grew with a longer processing time (Figs 3b and 3c). The relative concentration of sodium ( $3.61\% \pm 0.02\%$  after 90 seconds,  $2.01\% \pm 0.04\%$  after 270 seconds, and  $0.73\% \pm 0.02\%$  after 540 seconds) (Fig 3d) decreased with a longer processing time ( $P < .01$ ).

Since the peak of Ti2p shifted to the low-energy side and the peak of 453.4 eV attributed to titanium became apparent for each specimen after the 100-second argon sputtering (Fig 3a), the coating was removed and the "mother metal" was revealed. The relative concentrations of calcium and phosphorus decreased gradually with a longer sputtering time ( $P < .01$ ). However, even after the 100-second sputtering, peaks of calcium, phosphorus, and titanium were clearly observed on each specimen (Figs 3a to 3c). Since the relative concentrations of calcium and phosphorus were decreased by lengthening the sputtering time, and peaks of calcium, phosphorus, and titanium were seen simultaneously after sputtering, the boundary between the coatings and the titanium mother metal was not evident. Therefore, these coatings had a functional gradient.

The relative concentration of sodium of each specimen decreased gradually with a longer sputtering time ( $P < .01$ ). However, the peak of Na1s remained after 90 seconds of processing (Fig 3d).



**Fig 1** (Above) FTIR spectra of each specimen.



**Fig 2** (Right) XRD patterns of each specimen.

### Surface Topography

Photographs of each specimen under SEM are shown in Fig 4. Extremely small particles were observed on the specimen processed for 90 seconds (Fig 4a). Uniform and highly dense particles of coating were observed on the specimens after 270 seconds (Fig 4b) and 540 seconds (Fig 4c).

### Coating Thickness

The thickness of each coating on the specimens was approximately 1  $\mu\text{m}$ . In addition, the coatings were observed to adhere closely to the titanium substrates (Figs 4d to 4f).

## DISCUSSION

The present study evaluated the quality of the coating prepared by discharging in HBSS<sup>-</sup>. FTIR and XRD studies indicated that the crystallinity of the coating increased with a longer processing time. Since crystalline HA was detected on the specimens processed for 540 seconds, this condition was suitable for preparing an HA coating on a titanium surface by this method. Since  $\text{CO}_3^{2-}$  absorption peaks around  $1,500\text{ cm}^{-1}$  and  $860\text{ cm}^{-1}$  were detected, the  $\text{PO}_4^{3-}$  group of the coating was partially replaced with  $\text{CO}_3^{2-}$ , making the coating similar to human bone in that respect.<sup>15,16</sup> Furthermore, since the mean Ca/P ratio of the specimens processed for 540 seconds was the same as that of bone (1.71), the coating had a biomimetic property.

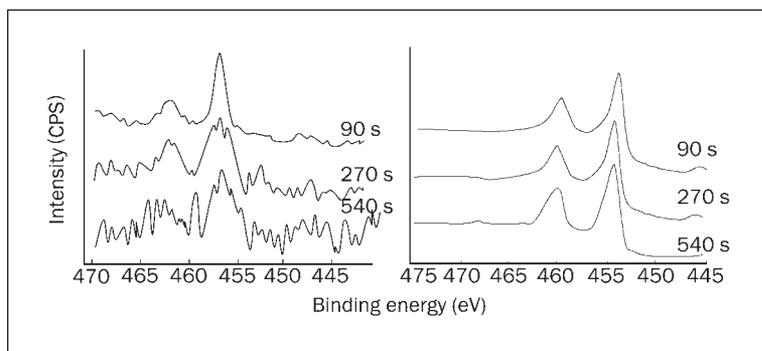
In the XRD study, the peak height of TiO increased with longer processing. Since the TiO suboxide has a high level of ionic activity compared with  $\text{TiO}_2$ , forming TiO seemed to contribute to the adsorption of the inorganic molecules in HBSS<sup>-</sup> and to adhesion between the coating and the titanium substrate.

Since the crystallinity of HA became evident as the processing time increased and the relative concentration of sodium decreased, HA nucleation depended strongly on the replacement of sodium ions with calcium ions. A previous study also demonstrated that a negatively charged titanium surface could enhance CaP deposition once initial sodium adsorption increased.<sup>17</sup>

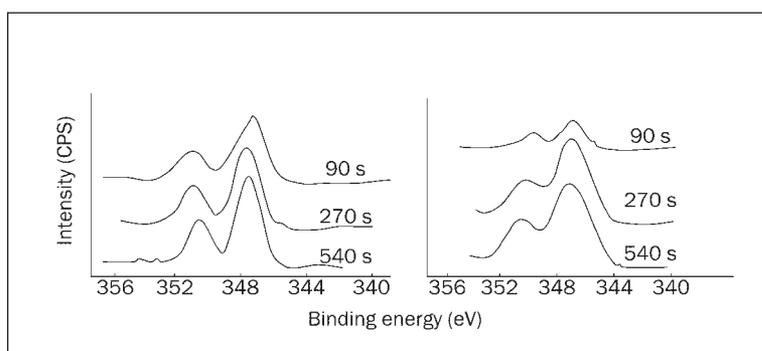
SEM observation demonstrated that each coating adhered closely to the titanium substrate. Since the thickness of the coating was constant at 1  $\mu\text{m}$  with different processing times, elements of the HA coatings accumulated not only on the titanium surface but also in the TiO film. In addition, elements of the coatings existed inside the titanium mother metal and decreased gradually in the XPS study. Therefore, the bonding state between the coating and titanium metal substrate was observed to be close, and these coatings had a gradient function.

Fujimori and colleagues have already demonstrated that porous CaP deposits are formed on titanium surfaces by discharging into an acidic-mixed CaP solution.<sup>11</sup> However, the chemical reaction in this technique is not accompanied by crystallization because of a lack of sodium adsorption in the TiO film introduced in this study.

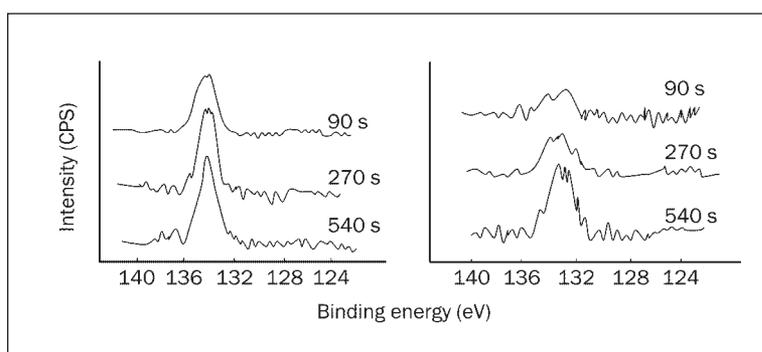
**Fig 3a** (Left) High-resolution spectra of Ti2p of each specimen. (Right) High resolution spectra of Ti2p of each specimen after 100-second argon sputtering.



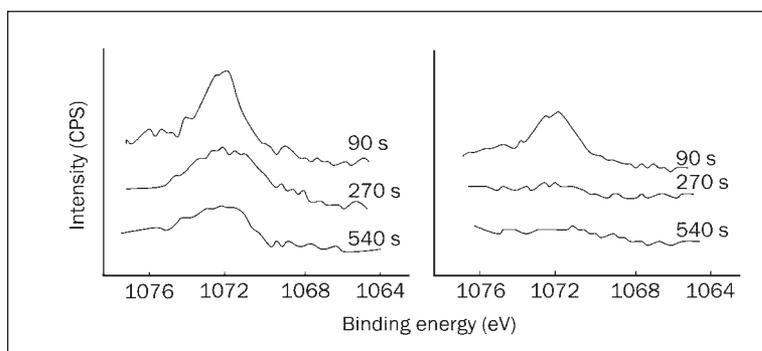
**Fig 3b** (Left) High-resolution spectra of Ca2p of each specimen. (Right) High resolution spectra of Ca2p of each specimen after 100-second argon sputtering.



**Fig 3c** (Left) High-resolution spectra of P2p of each specimen. (Right) High resolution spectra of P2p of each specimen after 100-second argon sputtering.



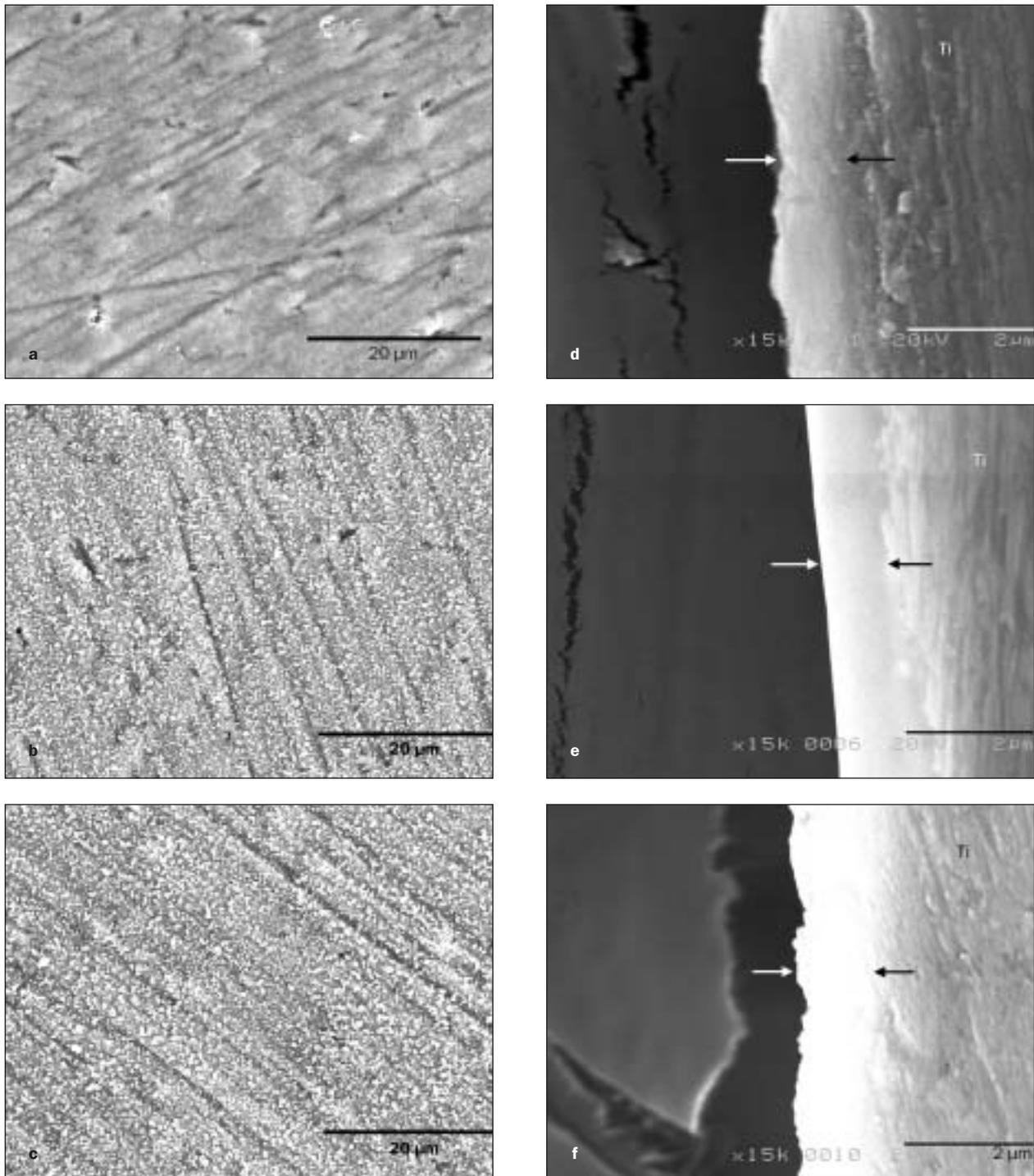
**Fig 3d** (Left) High-resolution spectra of Na1s of each specimen. (Right) High resolution spectra of Na1s of each specimen after 100-second argon sputtering.



Kishida also reported that adhesion between the HA coating and the titanium substrate was improved by a 2-stage discharging process using an acidic-mixed CaP solution.<sup>12</sup> However, this coating cannot be made thinner since it is formed through a thick, pretreated anodizing TiO<sub>2</sub> layer. In addition, the composition of the electrolyte causes

impurities in the coating (calcium compounds such as CaOH).

In the present study, since the TiO formed during discharging using a cathodic potential was thinner than that formed with anodizing in previous studies, a coating with a thickness of about 1 μm could be prepared in this study. Since a bonelike HA



**Fig 4** Photographs taken by SEM showing typical results. (a) Specimen processed for 90 seconds (original magnification  $\times 2,000$ ). (b) Specimen processed for 270 seconds (original magnification  $\times 2,000$ ). (c) Specimen processed for 540 seconds (original magnification  $\times 2,000$ ). (d to f) Cross sections of the specimens after 90 seconds, 270 seconds, and 540 seconds (original magnification  $\times 1,500$ ). The HA coating can be seen between the 2 arrows.

coating was obtained in HBSS<sup>-</sup> without calcium-compound impurities as in previous studies,<sup>11,12</sup> the ion concentration of this solution was appropriate.

These findings suggest that the bonelike HA coating prepared by discharging in HBSS<sup>-</sup> was suitable for coating implants, when compared with preparation of stoichiometric HA using an acidic-mixed CaP solution.<sup>11,12</sup>

The HA coating created on titanium surfaces by discharging in HBSS<sup>-</sup> can be explained as follows. The original TiO<sub>2</sub> layer on the titanium surface was broken by large cathodic potential during discharging in the solution. Subsequently, large amounts of sodium ions contained in the HBSS<sup>-</sup> were initially absorbed on the titanium mother metal while the TiO suboxide layer grew with discharging. Negative ions (PO<sub>4</sub><sup>3-</sup>, OH<sup>-</sup> and to some extent, CO<sub>3</sub><sup>2-</sup>) were subsequently absorbed on the surface. The Ca<sup>2+</sup> ions were induced on the absorption of those negative ions. Finally, the replacement of Na<sup>+</sup> ions by Ca<sup>+</sup> ions accelerated HA nucleation through the TiO layer, which had a high level of ionic activity. Therefore, the coating had a gradient function, with no boundary evident between the coating and substrate.

Further biologic studies are needed to evaluate the biocompatibility of HA-coated titanium prepared by this discharging method.

## CONCLUSION

The present study evaluated the quality of HA coating created by discharging in HBSS<sup>-</sup> and showed that a thin crystalline bonelike HA coating approximately 1 μm thick could be prepared on titanium surfaces by discharging in HBSS<sup>-</sup>. Furthermore, the HA coating on titanium was a functional gradient material.

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