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SURFACE MODIFICATION OF APATITE/TITANIUM COMPOSITE COATINGS DEPOSITED BY RF PLASMA-SPRAYING: IMPROVEMENT OF CHEMICAL RESISTANCE

Masahiko Inagaki, Atsushi Hozumi, Hiroki Okudera,
Yoshiyuki Yokogawa and Tetsuya Kameyama
National Industrial research institute of Nagoya 1-1 Hirate-cho,Kita-ku, Nagoya 462-8510, Japan
Fax: 81-52-916-6993, e-mail: minagaki@nirin.go.jp

To improve the chemical resistance of plasma-sprayed hydroxyapatite (HA) coatings on titanium, the surface modification of HA/Ti composite coatings on titanium substrates was carried out. An organosilane self-assembled monolayer was formed on each of the coated samples by chemical vapor deposition. The organosilane, 1H,1H,2H,2H-perfluorodecyltri-methoxysilane (FAS) was used as a precursor. The FAS-coated HA/Ti coatings became completely hydrophobic, with their contact angles changing from almost 0° before treatment to more than 130° afterwards. Solubility of bare HA/Ti and the FAS-coated HA/Ti coatings were evaluated in a 20 mM acetic acid/acetic acid sodium-salt buffer solution (6.0 pH) with 9% NaCl at 37 °C for 8 weeks. The total amount of calcium ions released from the FAS-coated HA/Ti coatings decreased compared with the bare HA/Ti coating. The HA/Ti composite coatings surface modified by FAS indicated improved chemical resistance under acidic conditions.

Key words: surface modification, self-assembled monolayer, plasma spraying, and hydroxyapatite coating

1. INTRODUCTION

Plasma-sprayed hydroxyapatite (HA) coated titanium materials have been used for medical and dental applications. [1] We have succeeded in the preparation of HA/Ti composite coatings of 150 μm in thickness having an adhesive strength of ca. 50 MPa. [2] However, long-term stability of these coatings has not been accomplished so far because of their low chemical resistance under acidic conditions, such as in the periodontal pockets (around 6.0 pH). [3] Therefore, solubility control of HA/Ti composite coatings is important when they are applied to implants. In this study, we report on the surface modification of HA/Ti composite coatings on titanium substrates by an organosilane self-assembled monolayer. The solubility of bare HA/Ti and FAS-coated HA/Ti coatings under the acidic condition was studied.

2. EXPERIMENTAL PROCEDURE

Commercial titanium plates (0.8 mm in thickness, ASTMB348-GR2) were polished with #400 SiC abrasive paper, ultrasonically washed in acetone and ethyl alcohol, and then dried in air. Hydroxyapatite powder (80 μm in diameter, Pentax) and titanium powder (< 325 mesh pass, 99.9%, Nilaco) were used as raw materials. A thermal plasma apparatus (Nihon Koshuha Co., Ltd., Japan) with a set of 4 MHz-35 kW power units (Nihon Koshuha Co., Ltd., Japan) was used. The experimental conditions for RF plasma spraying are summarized in Table I. The hydroxyapatite and titanium powder were fed axially into the plasma and deposited onto the Ti substrates. First, titanium powder was applied to a titanium substrate by RF plasma spraying process to obtain a roughened surface. Next, HA and Ti powders were applied by changing the feeding rate of HA and Ti powder. HA/Ti ratios of 0.36 and 1.4 were used at initial and the final stage, respectively. Then, HA powder was applied to the surface of the HA/Ti composite coatings. The HA/Ti composite coatings were evaluated by XRD. Orientation of crystals causes errors on calculation of the crystallinity. Therefore, the crystallinity of the surface HA layers in the HA/Ti composite coatings was estimated by HA coatings on substrates without Ti powder under the same experimental conditions. These HA coatings were peeled off, milled and then evaluated by XRD.

Surface modification of the HA/Ti composite coatings was carried out as follows. First, the surface of the HA/Ti composite coating were photochemically cleaned by exposure for 3 min to vacuum ultraviolet light (excimer lamp, Ushio Electric, UER 20-172 V, λ = 172 nm) in air. Organic contaminants on the coating surface were decomposed by direct photoexcitation and by the following oxidation with activated oxygen species. Next, an organosilane self-assembled monolayer was formed on each of these coated samples through chemical vapor deposition. An organosilane, that is, 1H, 1H, 2H, 2H-perfluorodecyltrimethoxysilane (FAS) was used as a precursor. Samples were placed in a vessel together with a glass container filled with FAS liquid. The vessel was sealed with a cap and then heated in an oven maintained at a temperature of 150 °C. The FAS liquid in the vessel vaporized and reacted with the OH groups on the coating. The molecules were chemisorbed onto the coating, resulting in the formation of a FAS monolayer [4]. To compare dissolution rates of the coatings in an acidic solution, both HA/Ti composite coatings without FAS coatings (non-modified HA/Ti coatings) and FAS-coated HA/Ti composite coatings (FAS-coated HA/Ti coatings) were prepared.

Table I Experimental conditions.

plasma power (kW)	11-27
plasma frequency (MHz)	4
plasma gas	argon/oxygen
flow rate of plasma gas (l/min)	50
pressure (Pa)	6.7×10^4
flow rate of carrier gas (l/min)	7
spray distance (cm)	28-35

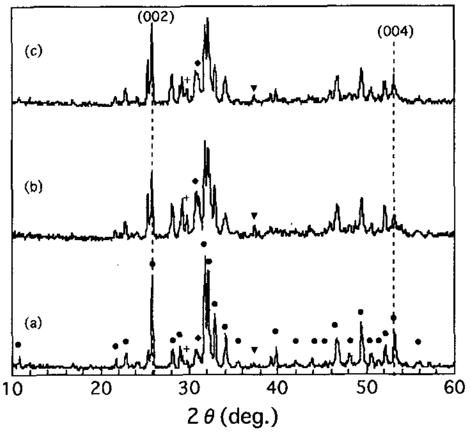


Figure 1 XRD patterns of coatings. ●: HA, ◆: TCP, +: 4CP, ▼: CaO.

Samples were kept in 10 ml of acetic acid/acetic acid sodium salt buffer solution (20 mM and 6.0 pH) with 9% NaCl at 37 °C. The buffer solutions were changed every week. Concentration of Ca^{2+} ions in the buffer solutions was determined by ion chromatograph (model DX-120, Dionex) with an analytical column (IonPac CS12A, Dionex) and a guard column (CG12A, Dionex). 20 mM methanesulfonic acid solution (Kanto-Kagaku P/N 50506003, dedicated to the column) was used as the eluent.

After immersion for a period of 12 weeks, the specimens were removed from the buffer solutions, gently rinsed with distilled water, and dried in air. The morphology of the coatings before and after immersion in the buffer solutions was observed by scanning electron microscopy.

3. RESULTS AND DISCUSSION

XRD patterns (Fig. 1) of as-prepared coating showed that the HA coatings had an apatite structure with a preferred orientation of (001). Minute X-ray peaks ascribable to tetracalcium phosphate (4CP), tricalcium phosphate (TCP) and calcium oxide (CaO) were also observed. The observed diffraction intensities of those additional phases were remarkably high in the case of spraying with RF power of above 17 kW. This observation indicates that a part of the HA powder decomposed in the plasma flame, particularly at RF powers of more than 17 kW. The crystallinities of the coatings sprayed at 12, 17 and 27 kW were 81.8, 68.0 and 70.3%, respectively. The crystallinity of the coatings decreased with increasing RF power. The FAS-coated HA/Ti coatings became completely hydrophobic with their contact angles changing from almost 0° to more than 130° afterwards.

The amount of released Ca^{2+} ions to the buffer solutions par the coating of 1 cm^2 for periods of a week is represented in Figure 2. The amount of released Ca^{2+} ions from coatings was decreased with the passage of time The release profiles of Ca^{2+} ions for coatings were influenced by the surface modification as well as RF power of the plasma spraying. The amounts of released Ca^{2+} ions from the coatings decreased with the passage of time. Dissolve rates of the FAS-coated HA/Ti coatings were reduced compared with the non-modified coatings in initial period of 2 weeks. After this period, there was no significant difference in the amounts of released Ca^{2+} ions between the FAS-coated and the non-modified coatings.

Figure 3 shows the cumulative amounts of released Ca^{2+} ions. The total amounts of released Ca^{2+} ions from the non-modified HA/Ti coatings sprayed at 12, 17 and 27 kW for periods of 8 weeks were 3.03, 3.53 and 1.88 mg, respectively. In the case of the FAS-coated specimens, the total amounts of released Ca^{2+} ions from the coatings sprayed at 12, 17 and 27 kW for same periods were 2.75, 3.01 and 1.52 mg, respectively. The decrease of released Ca^{2+} ions from the FAS-coated HA/Ti coatings indicate that chemical resistivity was increased by FAS coating.

Figure 4-6 shows SEM images of the coatings before and after immersion in the buffer solution. As sprayed, the coatings show a rough, heterogeneous, partial melt-like texture. These textures were similarly observed in the FAS-coated samples before immersion. After immersion for a period of 12 weeks, crater-like structures were observed in everywhere of the non-modified coatings. In the case of the surface modification by FAS, above surface damage relatively decreased as compared with the non-modified coatings. Figure 7 shows SEM images of the non-coated HA/Ti coatings and the FAS-coated HA/Ti coatings after immersion in detail. In the FAS-coated HA/Ti coatings, glass-like textures which indicated by 'G' in Fig.7b were observed while these textures were not observed in the non-coated HA/Ti coatings. These images and the release profiles of Ca^{2+} ions (Fig. 2) imply that the

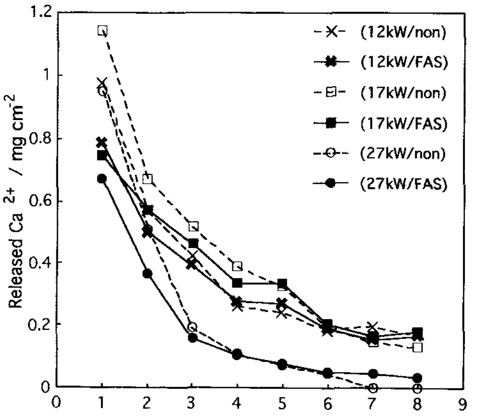


Figure 2 Amounts of the released Ca^{2+} ions for each 1 week period.

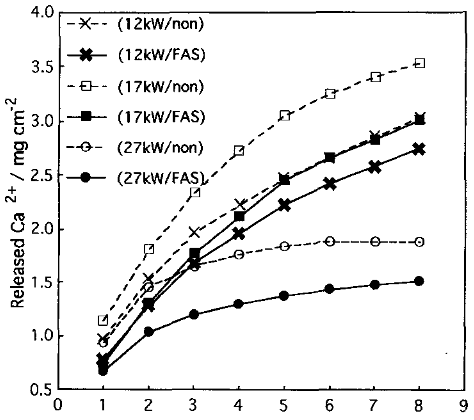
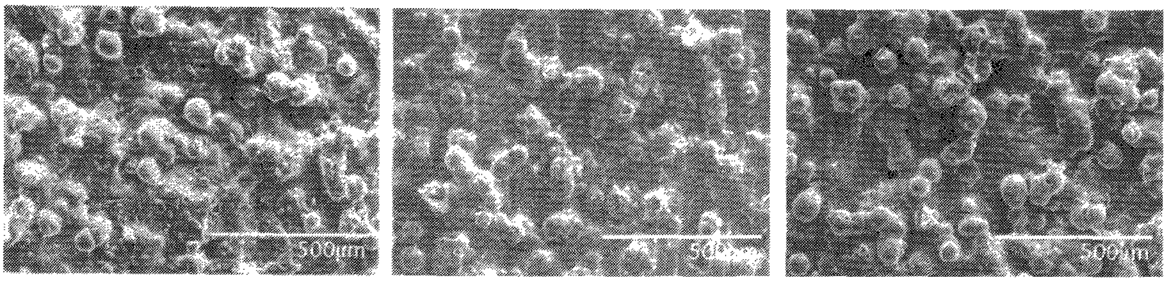
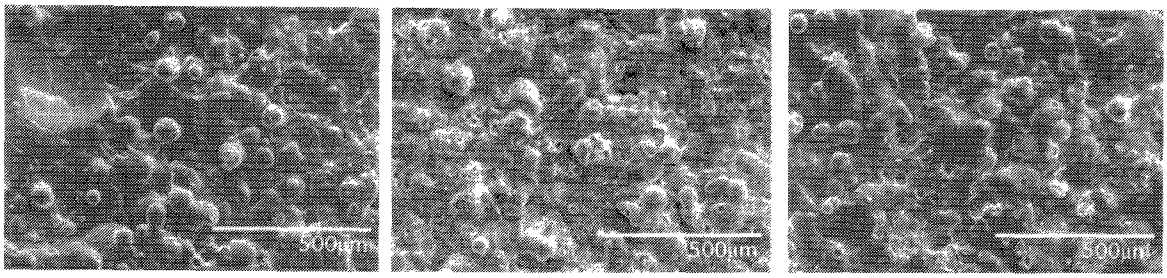


Figure 3 Cumulative amounts of the released Ca^{2+} ions.



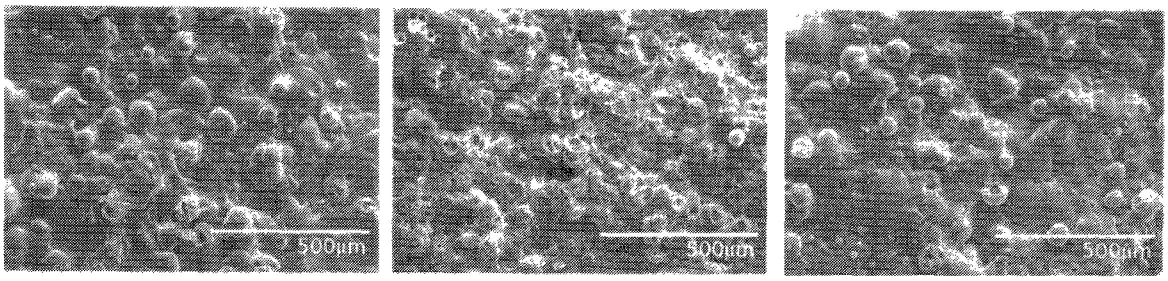
(before) (after immersion/non-coated) (after immersion/FAS coated)

Figure 4 Change in surface of the coatings sprayed at 12 kW before and after immersion in buffer solution.



(before) (after immersion/non-coated) (after immersion/FAS coated)

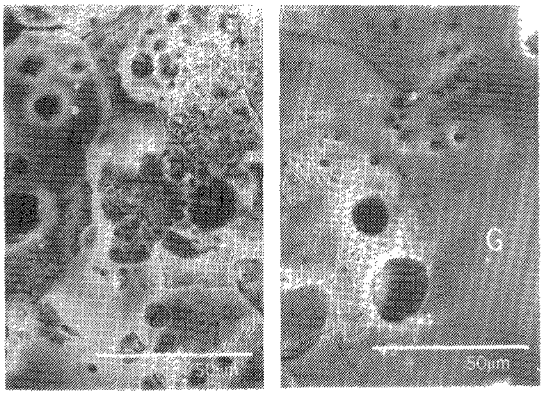
Figure 5 Change in surface of the coatings sprayed at 17 kW before and after immersion in buffer solution.



(before) (after immersion/non-coated) (after immersion/FAS coated)

Figure 6 Change in surface of the coatings sprayed at 27 kW before and after immersion in buffer solution.

dissolution of the coatings occurred mainly in the thin amorphous layer at surface of coatings. In the case of the FAS-coated HA/Ti coatings, incomplete dissolution of this amorphous layer may be caused by improvement of the chemical resistance of the surface of the coatings. The total amounts of released Ca^{2+} ions (Fig. 3) and the release profiles (Fig. 2) shows no relations with the crystallinity of coatings. In this study, the amounts of released Ca^{2+} ions from coatings may depend on the specific surface area of the coatings.



(a) (b)

Figure 7 SEM images of the coatings sprayed at 27 kW after immersion in buffer solution: (a) non-coated and (b) FAS-coated HA/Ti coatings.

4. CONCLUSIONS

Surface modification of HA/Ti composite coatings on titanium substrates was carried out. The amounts of released Ca^{2+} ions from FAS-coated HA/Ti coatings decreased as compared with the non-modified coatings in the initial few weeks. The total amounts of released Ca^{2+} ions also decreased in the case of the surface modification by FAS. A reduction of damage at the surface of the coatings, due to the immersion in acidic solution was showed by SEM observations. The surface modified HA/Ti composite coatings using FAS indicated improved chemical resistance under the acidic condition.

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