

Coating of hydroxyapatite films on titanium substrates by electrodeposition under pulse current

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Titanium (Ti) metal substrates were etched in sulfuric acid (H_2SO_4) with concentrations of 25, 50, 75 and 97% at 60°C for 30 min. Hydroxyapatite (HA) films were deposited onto unetched and etched substrates by an electrodeposition method under a pulse current. The electrolyte was metastable calcium phosphate solution that had 1.5 times the ion concentrations of human body fluid, but did not contain magnesium ion at 36.5°C. Deposition times were 90 min. We used the average current density of 0.01 A/cm² and ON time equal to OFF time of 15 s. In the electrodeposition, hydrogen was incorporated into the surface of the Ti substrates to form titanium hydride (TiH_2) on the substrate surfaces. After the electrodeposition, all specimens were heated at 600°C for 60 min. The adhesion between apatite and substrates were greatly improved by the heat treatment for the substrates etched in 50 and 75% H_2SO_4 . It is considered that in these specimens the anchoring effect due to the microstructural roughness formed by etching was enhanced by the shrinking of HA crystals during the heat treatment.

Key-words : Apatite, Titanium, Electrodeposition, Pulse current, Acid etching, Heat treatment

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1. Introduction

Titanium (Ti) metal and its alloys are widely used for orthopedic and dental applications because they exhibit high mechanical properties and biocompatibility.¹⁻³⁾ Ti metal has a passive layer of TiO_2 on its surface, which is responsible for its chemical stability and thereby its biocompatible characteristics. This oxide layer has naturally a thickness of a few nanometers but could be thickened to few micrometers by chemical and thermal treatments.⁴⁾ Although Ti metal is biocompatible, it is not bioactive and hence could not directly bond to living bones. In order to improve its bone-bonding property, hydroxyapatite (HA) coatings have been applied on to Ti implants.⁵⁾ Several coating methods, such as plasma spraying,⁶⁾ biomimetic precipitation⁷⁾ and electrodeposition,⁸⁾ have been successfully used to deposit a HA layer on Ti or titanium alloy implants. Each of these methods has some advantages and drawbacks. Among these coating techniques, only the plasma spraying of HA is clinically used. However, the high temperature of the plasma flame may give adverse effects on the structure of the implant and the homogeneity of the coating to result in the delamination of the coating.⁹⁻¹¹⁾

The electrodeposition method is an alternative process that uses aqueous solutions at low temperatures, which hardly give adverse effects on the structure of the implant and can be applied to complex shapes.¹²⁾ However, this method results in an increasing pH at the interface between Ti and electrolyte due to the electron incorporation to form OH^- ions and H_2 through water reduction. The H_2 gas evolution at the interface leads to a heterogeneous coating.¹²⁾ In addition, adhesive strength between the apatite and substrate is often low. Therefore, in order to solve the above problems, new approaches are needed in the electrodeposition method. In the process of metallizing plating, the Ti metal has been treated by sulfuric acid (H_2SO_4) before plating in order to

improve adhesive strength,¹³⁾ and pulse current has been employed in order to obtain deposits with a finer grain size, higher purity and smoother surface.¹⁴⁾ In this study, Ti substrates were previously subjected to acid etching, and then the electrodeposition in metastable calcium phosphate solution under pulse current. The surface structural changes of the substrates by the acid etching and the subsequent electrodeposition were fundamentally investigated, and the adhesion between deposited HA and substrates were qualitatively evaluated.

2. Experimental

Rectangular specimens of Ti substrates (purity: 99.5%, The Nilaco Corporation, Tokyo) with $10 \times 10 \times 1$ mm³ in size were abraded with #400 diamond plate, and then washed with acetone, ethanol and ultra-pure water in an ultrasonic cleaner.

Before the electrodeposition, Ti substrates were etched in 30 cm³ of sulfuric acid with concentrations of 25, 50, 75 and 97% at 60°C for 30 min. H_2SO_4 with concentrations of 25 and 75% was prepared by diluting 50 or 97% H_2SO_4 (Nacalai Tesque Inc., Kyoto, Japan) with ultra pure water. After the etching, the specimens were washed with ultra-pure water.

Electrodeposition was performed in a two-electrode cell configuration. The Ti specimens were used as cathode, and a platinum plate (HX-C2, Hokuto Denko Corp., Tokyo) was used as the counter electrode. The pulse current was applied by a function generator (Agilent 33120A, Agilent Technologies Inc) between the two electrodes. The average current density was 0.01 A/cm² and ON time was equal to OFF time of 15 s. The electrolyte was 60 cm³ of 1.5SBF (simulated body fluid) without magnesium (Mg^{2+}) ion at 36.5°C. **Table 1** shows ion concentrations and the pH of human blood plasma and some forms of SBF. Ion concen-

Table 1. Ion Concentrations and pH of Human Blood Plasma and Some Forms of SBF

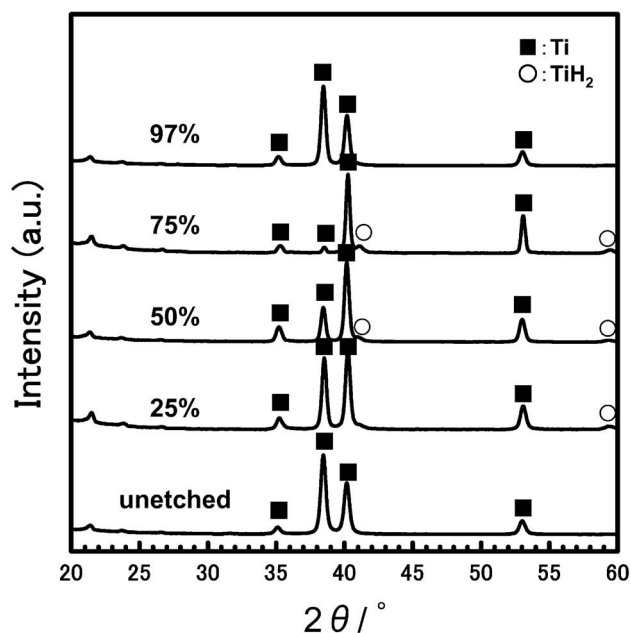
Ion	Ion Concentration (mol/m ³)			
	Blood Plasma	1.0 SBF	1.5 SBF	1.5 SBF without Mg ²⁺
Na ⁺	142.0	142.0	213.0	213.0
K ⁺	5.0	5.0	7.5	7.5
Mg ²⁺	1.5	1.5	2.3	0
Ca ²⁺	2.5	2.5	3.8	3.8
Cl ⁻	103.0	147.8	221.7	217.2
HCO ₃ ⁻	27.0	4.2	6.3	6.3
HPO ₄ ²⁻	1.0	1.0	1.5	1.5
SO ₄ ²⁻	0.5	0.5	0.8	0.8
pH	7.2-7.4	7.40	7.40	7.40

Table 2. Amounts of Reagents for Preparation of 1.5SBF Without Mg²⁺ Ions

	Reagent	Amount / g	Purity
1	NaCl	11.994	99.5%
2	NaHCO ₃	0.525	99.5%
3	KCl	0.336	99.5%
4	K ₂ HPO ₄ ·3H ₂ O	0.342	99.0%
5	1.0M-HCl	48 cm ³	-----
6	CaCl ₂	0.417	95.0%
7	Na ₂ SO ₄	0.107	99.0%
8	((CH ₂ OH) ₃ CNH ₂)	9.086	99.0%
9	1.0M-HCl	~15 cm ³	-----

trations and pH of SBF were nearly equal to those of human blood plasma.¹⁵⁾ In this study, in order to enhance the growth of hydroxyapatite crystals, the ion concentration are increased up to 1.5 times of normal SBF, but Mg²⁺ ion, which is an inhibitor of hydroxyapatite precipitation and growth,¹⁶⁾ is eliminated in the electrolyte. **Table 2** shows amounts of reagents for the preparation of 1.5 SBF without Mg²⁺ ion. This electrolyte was prepared by dissolving reagent grade chemicals of NaCl, NaHCO₃, KCl, K₂HPO₄·3H₂O, CaCl₂ and Na₂SO₄ (Nacalai Tesque Inc., Kyoto) in ultra-pure water. The pH of the electrolyte was adjusted to 7.40 with tris(hydroxymethyl)aminomethane ((CH₂OH)₃CNH₂) and 1.0 mol/dm³-HCl aqueous solution (Nacalai Tesque Inc., Kyoto) at 36.5°C. The deposition times were 90 min. After the electrodeposition, the specimens were gently washed with ultra pure water, and then they were heated at 600°C for 60 min in an electric furnace (MMF-1, AS ONE, Tokyo).

The surface structure of the specimens was investigated by field emission scanning electron microscopy (FE-SEM; S-4500, Hitachi Ltd., Tokyo), thin-film X-ray diffraction (TF-XRD, Rigaku RINT-2500, Tokyo) and Fourier Transform Infrared Spectrophotometer Attenuated Total Reflectance (FT-IR ATR; Nicolet Magna 860, Thermo Electron K.K., Kanagawa). The surface roughness (arithmetic average roughness: R_a and ten-spot average roughness: R_z) of the substrates was measured by Atomic Force Microscope (AFM, SPA300, Seiko Instruments Inc., Toyko).

Fig. 1. TF-XRD patterns of Ti substrates unetched and etched in H₂SO₄ with various concentrations.

The adhesion between apatite and substrates was evaluated using a Scotch[®] tape (810, Sumitomo 3M Limited, Tokyo).

3. Results and discussion

Figure 1 shows TF-XRD patterns of Ti substrates unetched and etched in H₂SO₄ with various concentrations. In all patterns, the diffraction peak assigned to the Ti (100) plane, the one assigned to Ti (002) plane, the one assigned to Ti (101) plane and the one assigned to Ti (102) plane were observed at 35.1°, 38.4°, 40.2° and 53.0° in 2θ, respectively. The intensity of the Ti (002) plane decreased with increasing the concentration of H₂SO₄ up to 75%. In the patterns of the substrates etched in 25, 50 and 75%, the diffraction peak assigned to TiH₂ (110) plane and the one assigned to TiH₂ (200) plane were also observed at 40.9° and 59.6° in 2θ, respectively.^{17),18)} This indicates that the (002) plane of Ti metal was selectively etched in 25, 50 and 75% H₂SO₄ and then surfaces of these substrates were partially hydrogenated by the H₂SO₄. In contrast, the diffraction pattern of the substrate etched in 97% H₂SO₄ was similar to that of the unetched substrate. This might be attributed to the fact that Ti metal hardly reacts with the oxidizing acid like strong sulfuric acid.¹⁹⁾

Figure 2 shows the ratio of the intensity of the diffraction peak assigned to the Ti (100) plane, the one assigned to Ti (002) plane, the one assigned to Ti (101) plane and the one assigned to Ti (102) plane (a), and the ratio of the two diffraction peaks assigned to (110) and (200) planes of TiH₂ (b) against the total intensities of all diffraction peaks. The ratio of the intensity of the Ti (002) plane decreased with increasing the concentration of H₂SO₄ from 25 to 75%. Instead, the ratio of the intensity of other planes of Ti metal and TiH₂ tended to increase with increasing the concentration of H₂SO₄ up to 75%. This indicates that other planes of Ti metal appeared with the progress of etching of Ti (002)

plane and the hydrogenation of Ti substrate progressed with increasing the concentration of H_2SO_4 up to 75%. From Figs. 1 and 2, it is considered that the optimal concentration might exist for the etching in H_2SO_4 solution.

Figure 3 shows FE-SEM photographs of the surfaces of the Ti substrates after the acid etching. While the surface of the specimen etched in 25% H_2SO_4 was partially unetched, the surfaces of specimens etched in 50 and 75% H_2SO_4 were uniformly etched (the data for the specimen etched by 50% H_2SO_4 were not shown).

Figure 4 shows the changes in the surface roughness (arithmetic average roughness: R_a , ten-spot average roughness: R_z) of the Ti substrate as a function of the concentra-

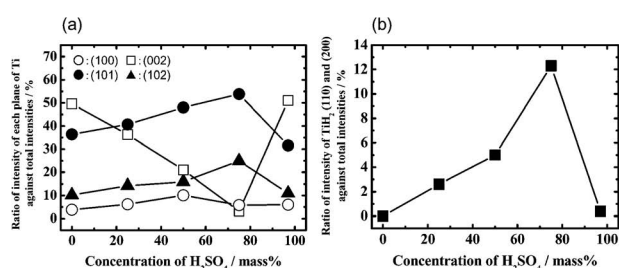


Fig. 2. Ratio of the intensity of the diffraction peak assigned to Ti (100) plane, the one assigned to Ti (002) plane, the one assigned to Ti (101) plane and the one assigned to Ti (102) plane (a), and the ratio of the two diffraction peaks assigned to (110) and (200) planes of TiH_2 (b) against the total intensities of all diffraction peaks.

tion of H_2SO_4 . Values of R_a and R_z tended to increase with increasing the concentration of H_2SO_4 until 75%. From Figs. 3 and 4, it was found that surface roughness kept proceeding with increasing the concentration of H_2SO_4 between 25 and 75% H_2SO_4 .

Figure 5 shows TF-XRD patterns of surfaces of Ti substrates after the electrodeposition (a) and subsequently heated at 600°C (b). In Fig. 5(a), the diffraction peaks ascribed to both HA and TiH_2 besides Ti metal were observed for all specimens. This indicates that HA was successfully deposited on the Ti metal surface but the surface of Ti metal was hydrogenated through the electrodeposition as well as the acid etching. Ti metal is known to be a good absorber of hydrogen.²⁰ Therefore, it is considered that the hydrogen gas that formed at the cathode²¹ was absorbed by Ti during the electrodeposition. In Fig. 5(b), while the diffraction peaks ascribed to both HA and Ti metals were still observed, but those ascribed to TiH_2 were disappeared for all speci-

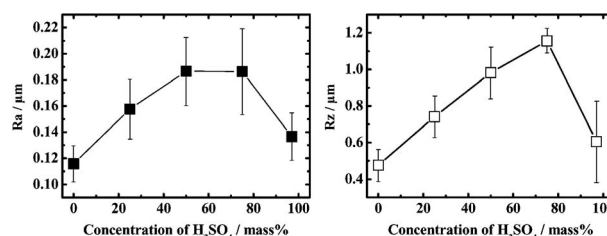


Fig. 4. Surface roughness (R_a and R_z) of the unetched Ti substrate and ones after the acid etching.

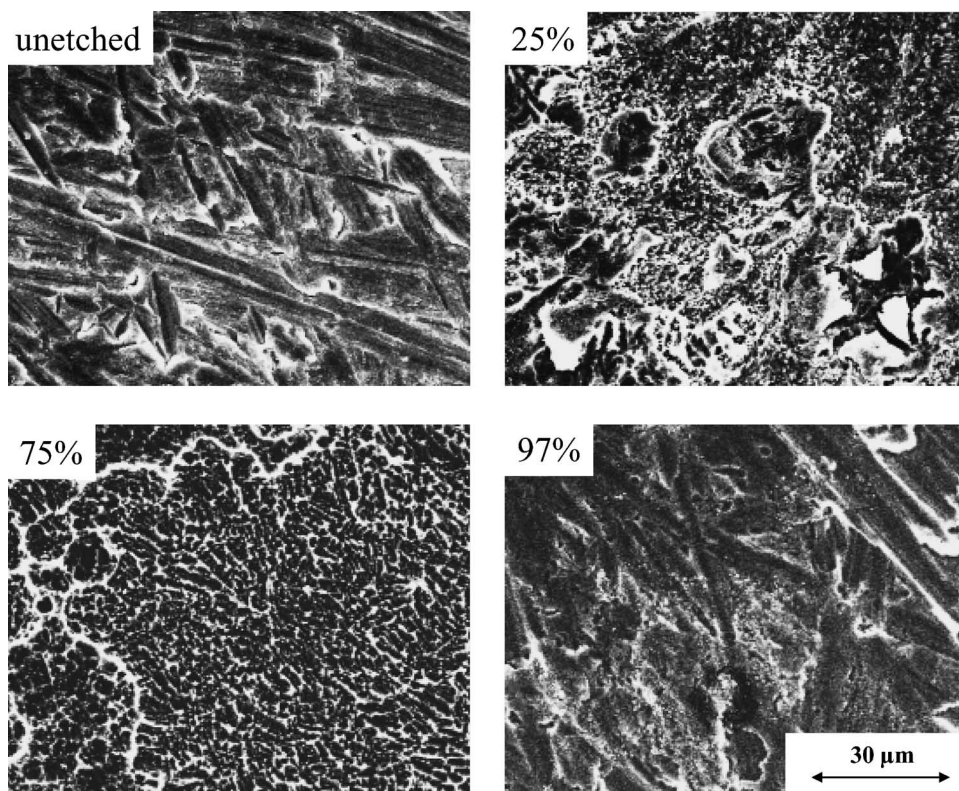


Fig. 3. FE-SEM photographs of the surfaces of the Ti substrates etched by various concentrations of H_2SO_4 .

mens. These results indicate that the dehydrogenation of all specimens occurred by the heat treatment.

Figure 6 shows FT-IR ATR spectra of Ti substrates after the electrodeposition (a) and subsequently heated at 600°C for 60 min (b). In Fig. 6(a), all spectra showed the PO_4^{3-} absorption bands^{22),23)} at 1100–1000, 960, 600 and 580 cm^{-1} , OH^- band at 1650 cm^{-1} , CO_3^{2-} bands between 1540–1350 cm^{-1} , and the CO_3^{2-} band²⁴⁾ or the HPO_4^{2-} band²⁵⁾ at 865 cm^{-1} . The existence of CO_3^{2-} band means that HA crystals including CO_3^{2-} were deposited onto the substrate by the electrodeposition. On the contrary, in Fig. 6(b), the OH^- band disappeared, and the $\text{P}_2\text{O}_7^{4-}$ absorption band newly appeared at 730 cm^{-1} . It is speculated that the moisture on

the surface and/or in the lattice vaporized and HPO_4^{2-} ion was formed into $\text{P}_2\text{O}_7^{4-}$ ion by the heat treatment.²⁶⁾

Figure 7 shows FE-SEM photographs of Ti substrates subjected to electrodeposition and subsequently heated 600°C. For each specimen, the left side is the FE-SEM photograph of the specimen after the electrodeposition and the right side is the one after the heat treatment. These photographs show that dense uniform layers were formed on the surfaces of all specimens. It was found from Figs. 5 and 6 that these layers might be HA. Compared with the specimens after the electrodeposition, the width of the cracks of HA crystals enlarged in the all specimens by the heat treatment. The

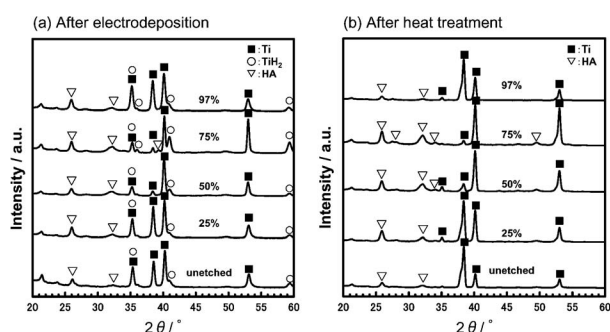


Fig. 5. TF-XRD patterns of surfaces of Ti substrates after the electrodeposition (a) and subsequently heated at 600°C (b).

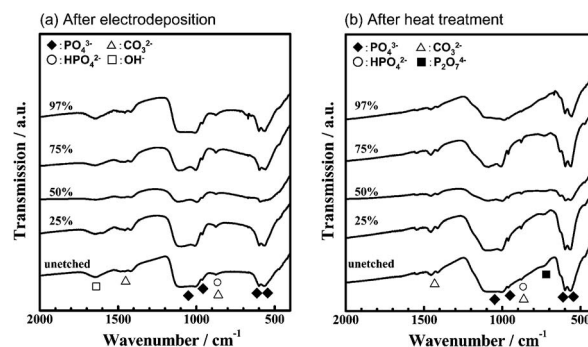


Fig. 6. FT-IR ATR spectra of Ti substrates after the electrodeposition (a) and subsequently heated at 600°C (b).

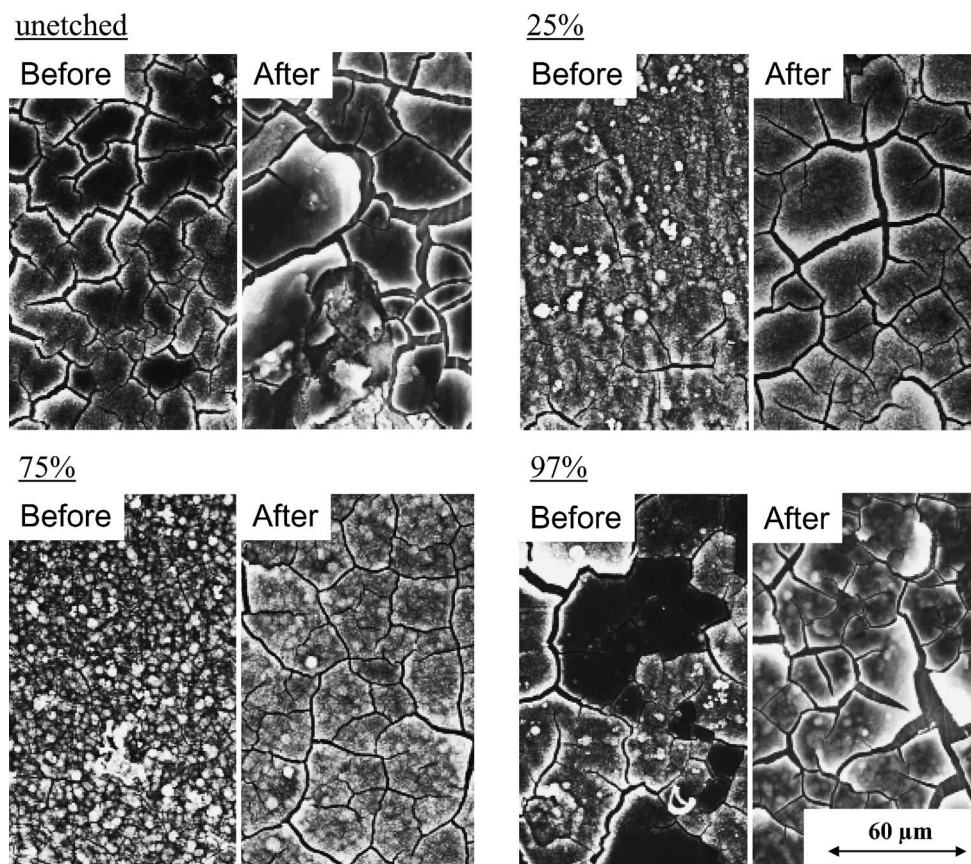


Fig. 7. FE-SEM photographs of Ti substrates after the electrodeposition (left) and subsequently heated 600°C (right).

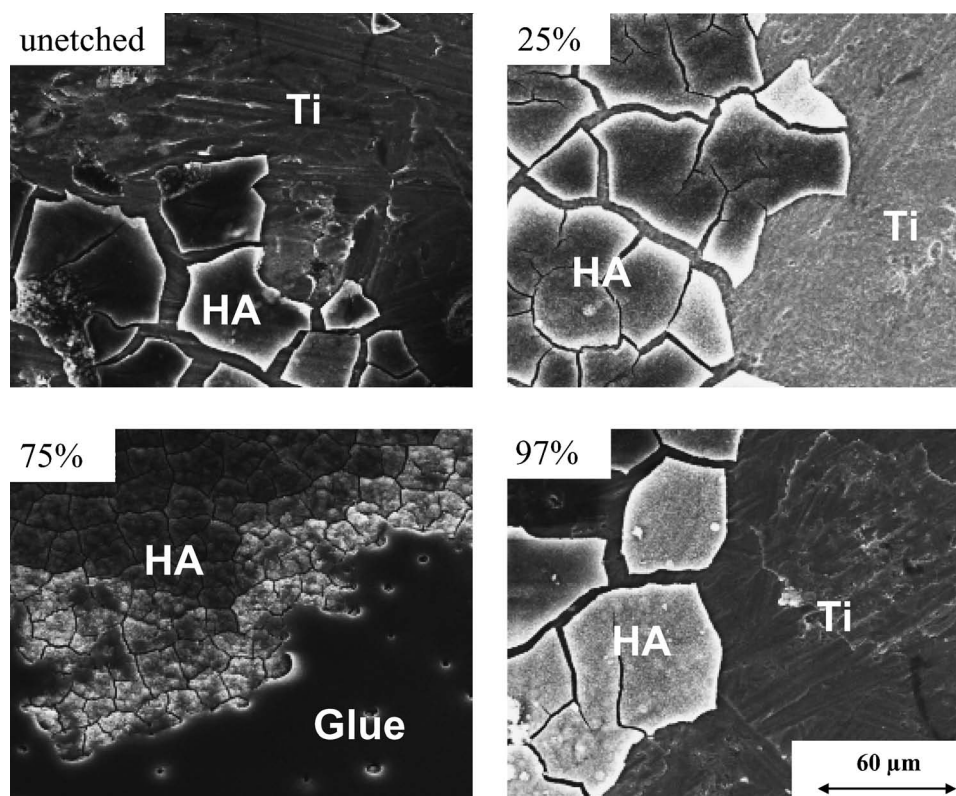


Fig. 8. FE-SEM photographs of the electrodeposited and heat-treated Ti substrates after the peeling test using Scotch® tape.

width of cracks of HA crystals on the substrates unetched or etched in 25 and 97% H_2SO_4 was larger than that on the substrates etched in 50 and 75% H_2SO_4 after the heat treatment (the data of the specimen etched in 50% H_2SO_4 were not shown). This indicates the degree of the shrinkage of HA crystals depended upon the concentration of H_2SO_4 . It is known that lattice water is escaping by heating below 400°C ,^{27),28)} accompanied by a slight decrease in the a -axis of HA crystal. From this result and Fig. 6(b), it is considered that the moisture on the surface and/or in the lattice vaporized during the heat treatment and then the width of the crack enlarged by the shrinkage with the decrease in a -axis of HA crystal.

Figure 8 shows FE-SEM photographs of the electrodeposited and heat-treated Ti substrates after the peeling test using Scotch® tape. While the deposited HA was easily peeled-off by the Scotch® tape for the substrates unetched and etched in 25 and 97% H_2SO_4 , it was not peeled-off and the glue of the Scotch® tape remained on the substrates etched in 50 and 75% H_2SO_4 (the data of the specimen etched by 50% H_2SO_4 were not shown). This indicates the adhesive strength of HA coating of the specimen etched in 50 and 75% H_2SO_4 was relatively high. It is considered that in these specimens the anchoring effect due to the microstructural roughness formed by the acid etching was enhanced with the shrinkage of HA crystals during the heat treatment. On the contrary, in the specimen treated by 25% H_2SO_4 , the unetched area of the substrate surface (see Fig. 3) might have prevented the anchoring effect, or surface roughness of the specimen treated by 25% H_2SO_4 might have been insufficient to enhance the anchoring effect (see

Fig. 4). In conclusion, when the Ti metals are previously etched in 50 or 75% H_2SO_4 , subjected to the electrodeposition and subsequently to the heat treatment, dense and uniform apatite layer with good adhesive properties can be formed onto the Ti substrates. It is believed that the present technique is useful for bioactive apatite coating onto metallic materials.

4. Summary

Ti metal substrates etched in H_2SO_4 with concentrations 50 and 75% were roughened uniformly. Hydroxyapatite (HA) films were deposited onto unetched and etched substrates by an electrodeposition method under a pulse current. The adhesive strength between HA and substrates etched in 50 and 75% H_2SO_4 were greatly improved by the heat treatment after the electrodeposition. It is considered that in these specimens, the anchoring effect due to the microstructural roughness formed by the acid etching was enhanced with the shrinkage of HA crystals during the heat treatment.

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