

Research Article

Novel Ceramic Coating on Titanium with High Mechanical Properties

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Received 11 November 2010; Accepted 2 December 2010

Abstract Phosphate coating layer was produced on titanium substrates by hydrothermal treatment with zinc phosphate solutions. Phosphatizing reaction produced zinc-titanium-phosphate coating layer on the surface by hydrothermal treatment at 250 °C. Ti substrate treated with low concentration of zinc phosphate solution for 14 h was not fully covered by the coating layer. On the other hand, surface coverage on Ti substrate treated with a high concentration of zinc phosphate solution for only 6 h was enhanced completely. SEM and XPS results indicated that the formation of the coating layer was inhibited by surface oxide layer. The coating layer was strongly attached on Ti substrate, moreover, the bonding strength between the coating layer and the Ti substrate was higher than the mechanical strength of binder.

Keywords titanium; zinc phosphate; coating; hydrothermal treatment

1 Introduction

Titanium (Ti) is the most widely used biomaterial for implant fabrication owing to its good corrosion resistance, heat and cold workability and excellent mechanical properties such as reasonable balance of high strength and low elastic modulus as compared with other metallic biomaterials. Its productions as implant have been used in orthopedics and dentistry [2,4]. There are several different kinds of surface treatments on titanium surface. These methods can be classified into two main groups, surface modification and surface coating. There are many kinds of surface modification methods, such as, hydrothermal treatment [9], ion sputtering [12], ion implanting [1], ion plating, ion beam mixing, anode oxidation [17], laser remelting [7], acid-etching [11,14], treatment with hydrogen peroxide [6], alkali and heat treatment [10] and so forth. Also there are surface coating methods such as plasma spraying [8,15], laser deposition [3], electrophoretic deposition [13], and sol-gel preparation [16]. The aim of this study is to establish a new method in order to fabricate strongly attached phosphate coating on titanium.

Therefore, hydrothermal treatment was employed. It is a useful method to acquire strong chemical bonding at the interface between coating layer and substrate because coating reaction in chemical solution can be carried out under the temperature higher than 100 °C.

2 Materials and method

Commercially obtained mirror polished pure titanium plates, 14.5 ϕ mm in diameter, were used as substrates. Substrates were first washed in acetone for 5 min followed by ultrasonic cleaning by distilled water for 5 min. The substrates were placed in Teflon vessel with stainless steel jacket containing zinc phosphate solutions. Then the vessel was kept at 200 °C and 250 °C for 6, 14 and 48 h for hydrothermal treatment. Chemical composition of the zinc phosphating solution is shown in Table 1.

Surface morphology and chemical composition of the coated layer was characterized by scanning electron microscopy (SEM) after gold coating and energy dispersed X-ray microanalysis (EDX). To evaluate the adhesive strength between the coating layer and the substrate, aluminum alloy rods with 4 mm diameter were bonded to both sides of the zinc phosphatized Ti substrate with acrylic super glue. Tensile testing was performed at a cross-head speed of 1 mm/min using a universal testing machine with a universal joint to ensure axial loading.

3 Results and discussion

Figure 1 shows SEM images of hydrothermally-treated Ti substrate with zinc phosphate solution-1 at 200 °C for 48 h.

	Solution-1	Solution-2
Phosphoric Acid (H ₃ PO ₄)	19.8 (ml/L)	39.6 (ml/L)
Zinc Oxide (ZnO)	14.7 (g/L)	29.4 (g/L)
Nitric Acid (HNO ₃)	23.5 (ml/L)	47.0 (ml/L)

Table 1: Chemical composition of the zinc phosphating solution.

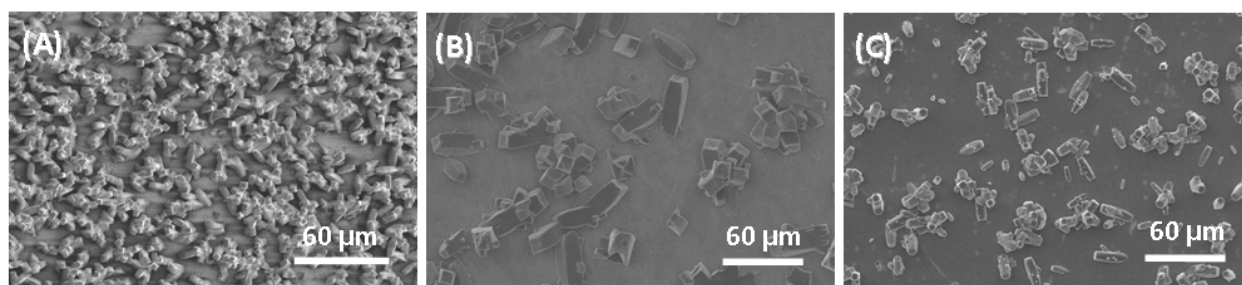


Figure 1: SEM images of hydrothermally-treated Ti substrate with zinc phosphate solution-1 at 200 °C for 48 h. Ti substrates with different pre-treatments were employed such as (A) without heat treatment, (B) heat-treated at 300 °C for 1 h and (C) heat-treated at 400 °C for 1 h.

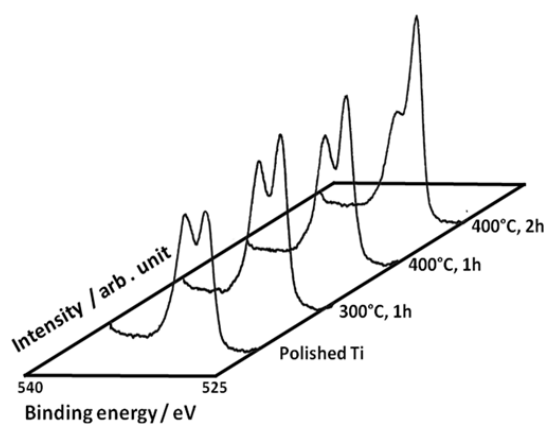


Figure 2: XPS spectra of polished Ti substrate and heat treated substrates at 300 °C for 1 h, 400 °C for 1 h and 400 °C for 2 h.

Ti substrates with different pre-treatments were employed such as (A) without heat treatment, (B) heat treated at 300 °C for 1 h and (C) heat treated at 400 °C for 1 h in order to investigate the effect of oxide layer on the substrate. Obviously, the surface could not be fully covered by the coating layer even if heat-treated Ti was used as a pre-treatment. Besides, the surface coverage was different between non-treated (Figure 1(A)) and heat-treated (Figures 1(B), 1(C)) substrates. As shown in Figure 1, surface coverage on heat-treated substrates was less than non-treated substrates.

Figure 2 shows XPS O1s spectra of Ti substrates before and after heat treatment at different temperatures. The major peak at 530.1 eV was assigned to the bulk oxygen atoms of titanium dioxide while another peak at 531.6 eV was assigned to physisorption of H₂O and oxygen atoms [5]. As shown in Figure 2, the peak intensity for TiO₂ increased with increasing heat-treatment temperature whereas the peak intensity for H₂O decreased with increasing heat-treatment temperature and duration for heat treatment. SEM and XPS results indicated that the formation of coating layer was inhibited by surface oxide layer.

Figure 3 shows SEM images and EDX spectra for hydrothermally-phosphatized Ti substrates treated at 250 °C for 6 h with solution-1(A), for 14 hrs with solution-2 (B), respectively. In Figure 3(A), Ti substrate treated at 250 °C for 14 h with solution-1 was still not covered by the coating layer. On the other hand, surface coverage on Ti substrate treated at 250 °C for only 6 h with solution-2 was enhanced completely as shown in Figure 3(B). EDX spectra from Figure 3(B) indicated that the coating layer has been composed of Zn, P, O and Ti elements.

Non-treated and phosphatized substrates were subjected to adhesive strength test in order to evaluate the adhesive strength between coating layer and substrate. Calculated average value for non-treated and phosphatized substrates was 16.7 ± 2.2 MPa and 15.7 ± 2.9 MPa, respectively. Figure 4 shows SEM image for phosphatized Ti substrates after adhesive strength test. Some broken parts in binder were clearly observed. However, the coating layer still remained on Ti substrate even after the adhesive test. This result indicated that the coating layer was strongly attached on Ti substrate. Moreover, the bonding strength between the coating layer and the Ti substrate was higher than the mechanical strength of binder.

4 Conclusions

Zinc phosphate coating layer was successfully produced on titanium substrate by hydrothermal treatment with zinc phosphate solution. The coating layer was composed of zinc, titanium and phosphate. The layer quickly and fully covered the titanium surface when high concentration of zinc phosphate solution was used for hydrothermal treatment. The formation of coating layer was inhibited by surface oxide layer. Adhesive strength test indicated that the coating layer was strongly attached on the titanium substrate.

Acknowledgment This project is supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan.

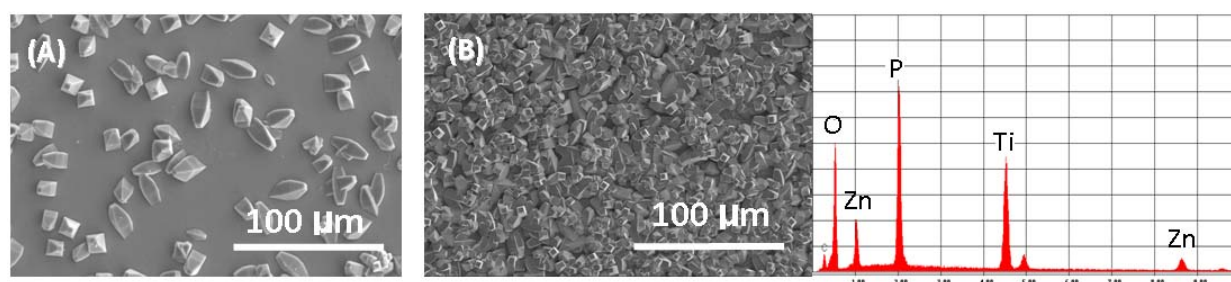


Figure 3: SEM images and EDX spectra for hydrothermally-phosphatized Ti substrates treated at 250 °C for 6 h with solution-1(A), and for 14 h with solution-2 (B), respectively.

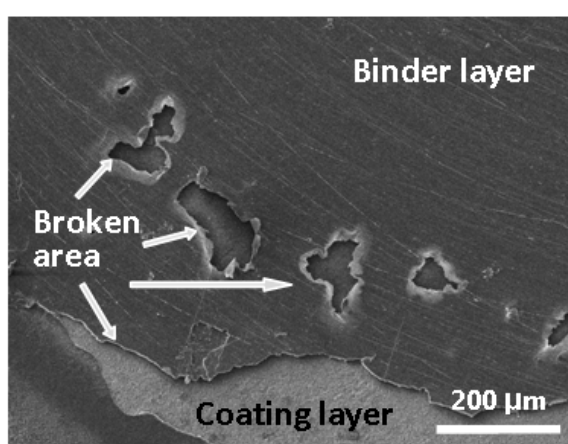


Figure 4: SEM image for phosphatized Ti substrates after adhesive strength test.

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