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Effect of Ti Intermediate Layer on Properties of HAp Plasma Sprayed Biocompatible Coatings

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The objective of this study was to improve properties of plasma sprayed HAp layer to titanium substrate by introducing an intermediate layer with two different methods. Before applying Zn doped HAp coating on titanium substrate, an intermediate layer was introduced by titanium plasma spray or titanium anodization. Heat treatments were conducted for some samples after titanium intermediate layer was formed. Zn doped HAp top layer was applied by plasma spraying. Three-point bending test and pull-off adhesion test were performed to determine the adhesion of Zn doped HAp coatings to substrates. Long-term credibility of Zn doped HAp plasma sprayed coatings on titanium was assessed by electrochemical impedance measurements in Hanks' solution. It was found that both titanium plasma sprayed and titanium anodized intermediate layer had excellent credibility. Strong adhesion to the titanium substrate was confirmed after 12 weeks of immersion for coating samples with titanium plasma sprayed intermediate layer. Samples with titanium anodized intermediate layer showed good bending strength. However, they showed relatively poor resistance against pulling off. The thickness of titanium anodized intermediate layer can be controlled much more precisely than that of plasma sprayed one, which is important for practical application.

Keywords: *Hydroxy apatite, Plasma sprayed coating, Intermediate layer, Titanium, Anodization*

1. Introduction

Metallic materials have played an important role in orthopedic and dental implants markets due to their excellent mechanical properties and relatively good stability inside human bodies especially in the case of titanium and its alloys. However, metallic implants have problems such as biocompatibility, osseointegration, corrosion and toxic metal ion release [1]. For solving these problems, many researchers have tried to find ways to improve metallic materials by applying biocompatible surface layers on metallic implants.

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp), which is the main inorganic component of bones and teeth, is a very promising candidate for the formation of biocompatible surface coatings on metallic implants. There are several coating techniques for applying a biocompatible HAp layer on the surface of metallic implants such as plasma spray, electrophoretic deposition, sputtering, Sol-Gel, etc. [2-6]. Plasma spray technique has been the only practical method for preparing commercial metallic implants coated with HAp. The advantage of plasma spraying is that it can get a relatively thick HAp coating layer and better adhesion to the metallic substrates. Also, the porous nature of plasma sprayed HAp coatings is very helpful for the growth of tissues inside HAp coating layer and consequently forming in a good environment for the osseointegration of the implant.

As a good biocompatible coating for metallic implants, the adhesion of coating layer to the metallic substrates is also very critical besides its biocompatibility. The development of biocompatible plasma sprayed HAp coatings has been carried out in our lab [7-11]. Our previous researches showed that the adhesion of HAp plasma sprayed coatings to titanium or stainless steel (SUS316L:17.75%Cr, 14.08%Ni, 0.018%C, etc.) can be improved greatly by introducing a Ti plasma sprayed intermediate layer [7]. Also, the effect of post heat treatment on both Ti intermediate layer and Zn doped HAp layer has been investigated. The adhesion of Zn doped HAp plasma coating had a slight decrease by post heat treatment on Zn doped HAp layers but remains in an excellent condition [12]. In this study, intermediate layers were prepared by titanium plasma spray and titanium anodization. The effect of the intermediate layers on the properties of plasma sprayed Zn doped HAp

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coatings has been investigated.

2. Experimental Methods

2.1 Preparation of Zn doped HAp plasma sprayed coatings

99.5% pure titanium was used as the metallic substrate for preparing Zn doped HAp plasma sprayed coatings. Round rods (ø 3 mm × 500 mm), rectangular rods (500 mm × 3 mm × 4 mm) and square plates (20 mm × 20 mm) were used for credibility tests (corrosion resistance monitoring), three-point bending tests and pull-off tests, respectively. All samples were polished by sand paper up to 1200 grit before shifting to the next process.

Intermediate layers were introduced by either titanium plasma spraying or titanium anodizing. For plasma spray process, a titanium intermediate layer was formed on titanium substrate by plasma spray at 400A, air atmosphere. The carrier gases for plasma spray process are argon and helium. The thickness of plasma sprayed intermediate titanium layer was controlled around 25 μm for each sample. After plasma spraying, heat treatment was conducted for some samples at 600 °C for 1 hour under argon atmosphere. In the process of titanium anodizing, samples were anodized in 5 M H_2SO_4 solution (cooled with 4 °C ice water) for 10 to 15 minutes. The anodizing current was adjusted from 50 mA to 130 mA according to the shape of the samples. After anodizing, all samples were dried for 24 hours at 80 °C. Sand blasting was conducted before or after the anodizing process to see the effect of the roughness on the adhesion. Table 1 and Table 2 show the conditions for preparing Zn doped HAp coatings with an intermediate layer of titanium plasma spray or titanium anodizing, respectively. Zn doped HAp coatings were applied on the top of intermediate layers for all samples. Post heat treatments were conducted for some coating samples at 600 °C, argon atmosphere for 1 hour (furnace cooling) as shown in Table 1 and Table 2.

Table 1 Heat treatment conditions for coatings with Ti plasma sprayed intermediate layer

Condition No.	Ti intermediate layer	Zn doped HAp layer
No.1	600 °C, 1 hour	600 °C, 1 hour
No.2	600 °C, 1 hour	as sprayed
No.3	as sprayed	600 °C, 1 hour
No.4	as sprayed	as sprayed

Table 2 Heat treatment conditions for coatings with Ti anodized intermediate layer

Condition No.	Anodizing condition	Zn doped HAp layer
No.5	Sandblast & 10 min	as sprayed
No.6	Sandblast & 10 min	600 °C, 1 hour
No.7	15 min & Sandblast	as sprayed
No.8	15 min & Sandblast	600 °C, 1 hour

2.2 Long-term credibility tests

Long-term credibility of Zn doped HAp plasma sprayed coatings was evaluated by electrochemical impedance measurements. The changes in impedance behavior and corrosion resistance were monitored by electrochemical impedance measurements in Hanks' solution at 37 °C for 12 to 16 weeks. A three-electrode configuration was used in this study. Platinum sheet and SSE (Ag / AgCl) were used as counter and reference electrode, respectively. A sinusoidal perturbation of 10 mV was applied and the frequency was scanned from 10^5 Hz to 10^{-2} Hz.

2.3 Adhesion tests

The adhesion of Zn doped HAp coatings was evaluated by two different methods. One is ASTM standard adhesion test with an adhesion tester called PosiTest AT. The pull-off strength of Zn doped HAp coating layer was measured for samples obtained under different conditions. Another adhesion test is three-point bending.

The surface morphology and cross section profile of Zn doped HAp plasma sprayed coating samples were observed by scanning electron microscope (SEM). The element distribution on the surfaces and cross sections was analyzed by EDS.

3. Results and Discussion

3.1 Long-term credibility of plasma sprayed Zn doped HAp coatings

Fig. 1 shows the impedance behavior in Hanks' solution for plasma sprayed Zn doped HAp coating with an intermediate layer prepared by titanium plasma spray. It can be seen that the impedance behaviors for samples prepared under condition of No.1 to No.3 (shown in Table 1) showed similar characteristic. Two components with different time constant were observed. One is at the relative high frequency area and the other is at low frequency area. In the case of condition No.4 under which heat treatment was not applied either to plasma titanium intermediate layer or to Zn doped HAp top layer, only one time constant at low frequency was observed. Therefore, it is considered that the heat treatment may have an effect on impedance behavior Zn doped HAp coatings with titanium plasma sprayed intermediate layer. The reason is not clear but

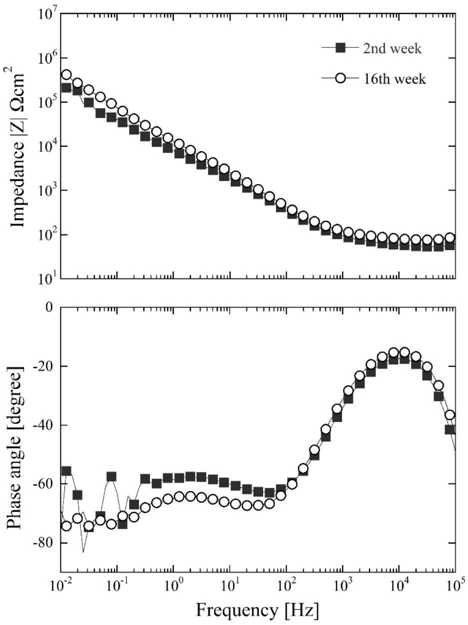

Fig. 1 Impedance behavior for Zn doped HAp plasma sprayed coating with Ti plasma sprayed intermediate layer after 2 weeks immersion in Hanks' solution at 37 °C. samples were prepared under conditions shown in Table 1.

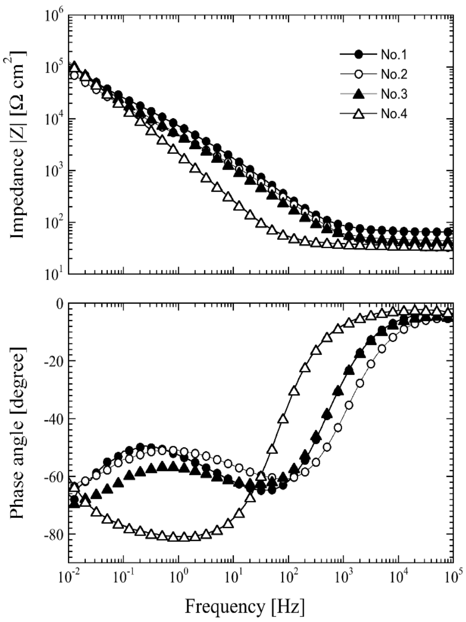

Fig. 3 Impedance behavior and its change in Hanks' solution at 37 °C for Zn doped HAp plasma sprayed coating with an intermediate layer prepared by titanium anodization. The sample was prepared under conditions of No.5 shown in Table 2.

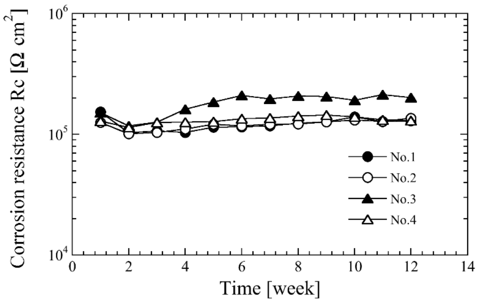

Fig. 2 Changes in corrosion resistance R_C for Zn doped HAp plasma sprayed coatings with Ti plasma sprayed intermediate layer in Hanks' solution at 37 °C. samples were prepared under conditions shown in Table 1.

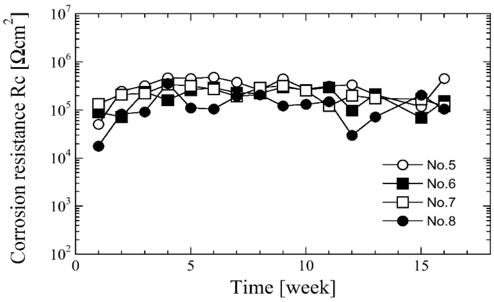

Fig. 4 Changes in corrosion resistance in Hanks' solution at 37 °C R_C for Zn doped HAp plasma sprayed coatings with an intermediate layer prepared by titanium anodization. The samples were prepared under the conditions shown in Table 2.

it is considered that the oxidation of titanium intermediate layer or the recovery of crystallinity of Zn doped HAp layer may contribute to it. The impedance behavior kept almost same for all samples during 12 weeks immersion, meaning that the Zn doped HAp coatings are stable.

The evaluation of credibility was carried out by monitoring the corrosion resistance R_C (impedance value at low frequency, 10^{-2} Hz). Fig. 2 shows the changes in corrosion resistance R_C for samples of whose titanium plasma sprayed intermediate layers were prepared under different conditions (shown in Table 1). After a slight drop during the first week immersion, the corrosion resistance for all samples increased gradually and became stable, indicating that all sample have excellent long-term credibility. It was found that heat treatment on titanium plasma had no positive effect on improving corrosion resistance of Zn doped HAp coating. On the other hand, heat treatment on Zn doped HAp layer is considered to be effective because it can improve the crystallinity of HAp from amorphous state (as spayed) to a crystal structure [7]. However, in the case of No.1, the application of heat treatment on both titanium plasma sprayed intermediate layer and Zn doped HAp layer did not improve the corrosion resistance further mainly because the twice heat treatment may cause more residual stress and micro cracks in coating layers. From the results of Fig. 2, it is concluded that the best condition for preparing Zn doped HAp plasma sprayed coatings is No.3 under which only heat treatment on Zn doped HAp layer was applied.

Besides titanium plasma sprayed intermediate layer, titanium anodization was also applied as an intermediate layer for Zn doped HAp coatings in this study. Fig. 3 shows the impedance behavior of plasma sprayed Zn doped HAp coating with an intermediate layer prepared by anodizing the surface of titanium substrate. Compared to Fig. 1, similar behavior was observed, meaning that the change of intermediate layer type did not affect the impedance behavior of Zn doped HAp coatings. Fig. 4 shows the changes in corrosion resistance R_c for samples with titanium anodized intermediate layers prepared under different conditions (shown in Table 2). It can be seen that the corrosion resistance for all samples increased with immersion time during the first 3 weeks and then became stable. Compared to the results of titanium plasma sprayed intermediate layer, the corrosion resistance is at the same level indicating that changing intermediate layer did not have obvious negative effect on corrosion resistance of Zn doped HAp coatings. However, under condition of No.8, the fluctuation of R_c was larger than No.5 to No.7 and those with titanium plasma sprayed intermediate layers (Fig. 2). Further investigation about the effect of parameters for anodizing process such as current control and time is needed.

3.2 Evaluation of Adhesion of plasma sprayed Zn doped HAp coatings

The adhesion of plasma sprayed Zn doped HAp coatings to titanium substrate was evaluated by two different tests. One is three-point bending test and another is pull-off test by using an ASTM standard device called PosiTest AT. Results of three-point bending test for Zn doped HAp plasma coatings on titanium with an intermediate layer prepared by either titanium plasma spray (No.1) or titanium anodizing (No.6 and No.7) are shown in Fig. 5. Photos for each sample in Fig. 5 were taken after the bending tests. It can be seen that there was no severe peeling off for all samples after a deformation with a displacement of 1.2 mm for every sample, meaning that all Zn doped coating samples tested have excellent adhesion and relatively good ductility. Compared to No.6 and No.7, sample prepared under No.1 condition showed a lower value of bending stress at final stage of deformation. Photo of sample No.1 after bending test showed small crack at the center of loading position and partially peeling off of Zn doped HAP layer around it was confirmed (slight color changing of the Zn dope HAp layer) while for samples prepared under No.6 and No.7 which prepared with titanium anodized intermediate layer, there was no cracking at the center and the bending stress was higher than that of sample No.1, indicating that there is no generation of cracking or peeling off even at a displacement of 1.2 mm. Therefore, it is considered that samples prepared with titanium anodized intermediate layer have higher bending strength than samples prepared with titanium plasma sprayed.

Pull-off tests for plasma sprayed Zn doped HAp coatings with titanium plasma sprayed intermediate layer were conducted in our previous studies [12]. In this study, pull-off tests were carried out for samples after 10 weeks immersion in Hanks' solution and the results and sample photos after pull-off test are shown in Fig. 6. From the photos in Fig. 6, the stripping happened at interface between Zn doped HAp top layer and titanium plasma sprayed intermediate layer. The adhesion strength for all samples is over 45 MPa and only tested areas were pulled off. It is concluded that there is no decreasing of adhesion

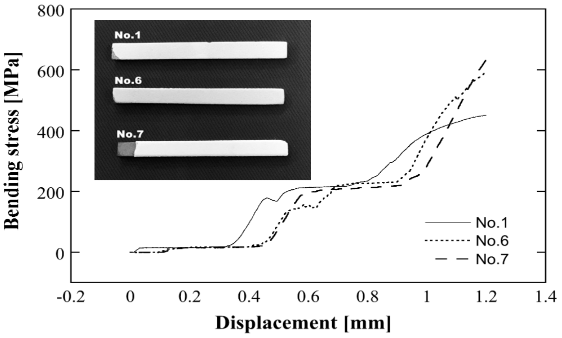

Fig. 5 Results of three-point bending test for plasma sprayed Zn doped HAp coatings under different conditions (shown in Table 1 and Table 2).

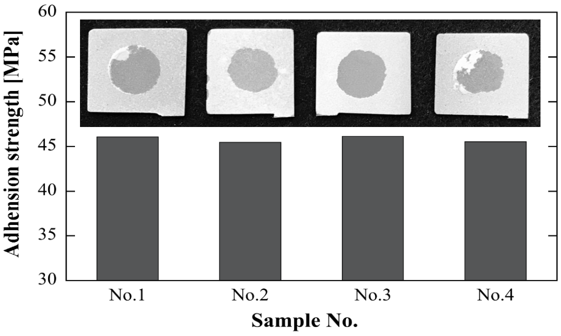

Fig. 6 Adhesion test results for plasma sprayed Zn doped HAp coatings after 10 weeks immersion in Hank's solution at 37 °C.

strength for all samples tested after 10 weeks immersion in Hanks' solution, indicating that the introduction of titanium plasma sprayed intermediate layer is very effective. On the other hand, for Zn doped HAp coating with intermediate layer prepared by titanium anodizing, only one sample was tested and the adhesion strength is 30 MPa, which is lower than that with titanium plasma sprayed intermediate layer.

3.3 The characteristics of intermediate layers prepared by titanium anodization

Plasma sprayed titanium intermediate layer was first introduced by our research group for improving the corrosion resistance of metallic substrates such as stainless steel. It was found later that it also can improve the adhesion of HAp coating layer to metallic substrates [7]. From results of this study (Fig. 6), it was confirmed that there was no degradation of the adhesion of Zn doped HAp layers to titanium substrates during long term immersion tests in Hanks' solution. However, the thickness of plasma sprayed titanium intermediate layer is generally over 20 μm because a uniform layer cannot be formed perfectly when the thickness is under 20 μm due to the difficulties of controlling the thickness precisely during plasma spray process. Also, an intermediate layer with a thickness more than 20 μm is sometimes unacceptable for certain practical applications.

A new approach of preparing intermediate layer was conducted in this study by directly anodizing the surface of titanium substrate. Fig. 7 shows the X-ray diffraction result of titanium substrate after being anodized. It can be seen that the surface composition is a mixture of two types of titanium oxide, rutile and anatase. Surface morphology of titanium anodizing is shown in Fig. 8. Porous TiO_2 layer was formed and the average diameter of the pores is less than 500 nm. The TiO_2 layer with micro porous structure shown in Fig. 8 formed evenly on the surface of titanium substrate. A typical cross section and the elements distribution are shown in Fig. 9. As shown in Fig. 9, the thickness of TiO_2 layer is estimated to be around 1.2 μm. There is no cracking or peeling off at the interface of titanium substrate / TiO_2 or TiO_2 / Zn doped HAp layer.

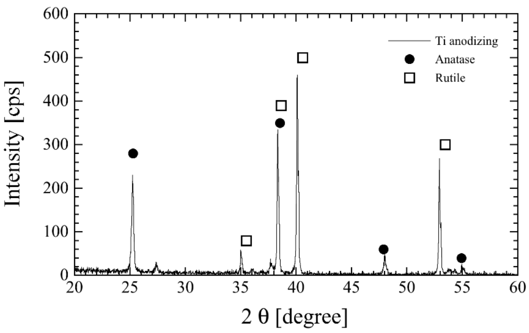

Fig. 7 X-ray diffraction result for the surface of titanium substrate after being anodized in H_2SO_4 solution for 15 minutes.

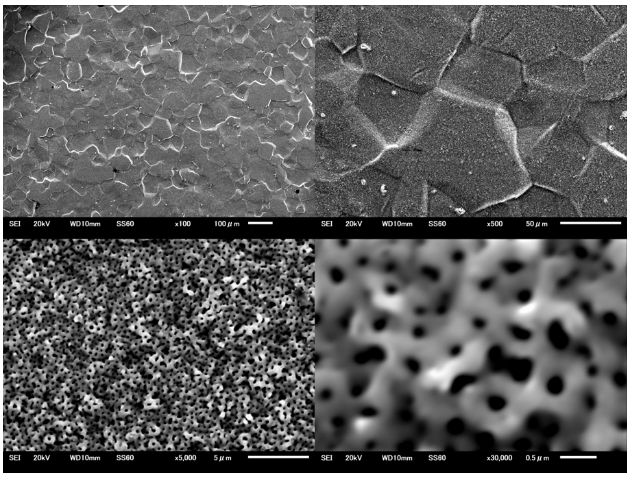

Fig. 8 Surface morphology for titanium substrate after being anodized in H_2SO_4 solution for 15 minutes.

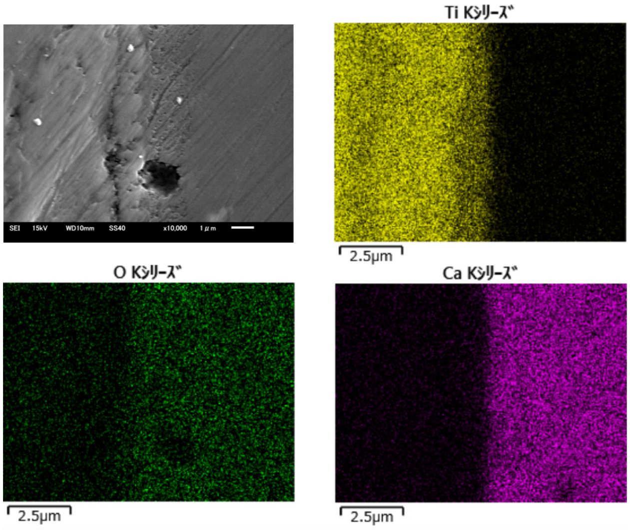

Fig. 9 Cross section profile by SEM and elements distribution by EDS for plasma sprayed Zn doped HAp coating with an intermediate layer prepared by titanium anodizing in H_2SO_4 solution for 15 min.

4. Conclusions

Two kinds of intermediate layer were introduced for preparing Zn doped HAp plasma sprayed coatings. For Zn doped HAp coatings with titanium plasma sprayed intermediate layer, excellent credibility was confirmed during 16 weeks immersion in Hank's solution. The adhesion to titanium substrate kept in a good level after long-term immersion. On the other hand, Zn doped HAp coatings with titanium anodized intermediate layer also showed good long-term credibility similar to samples with titanium plasma sprayed intermediate layer. The adhesion evaluation showed good bending strength but relatively poor peeling off resistance. The reason is not clear but the porous structure may contribute to the relatively poor resistance against the pulling off. Since the thickness of titanium anodized intermediate layer can be controlled much more precisely than that obtained by plasma spray process, titanium anodizing process is considered to be a promising method of introducing intermediate layer for improving the performance of HAp coatings on titanium or titanium alloys.

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