

Microstructures at/around Interface between Plasma Spray Coated Hydroxyapatite and Ti Alloy*

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Microstructures of the interface between plasma spray coated hydroxyapatite (HAp) and Ti-alloy substrate have been investigated mainly by means of transmission electron microscopy. The results obtained are as follows; Interface of HAp/Ti-alloy is winding at an interval of about 100 μ m and thickness of HAp coating is about 50 μ m. HAp coating exhibits a high crystallinity. Al₂O₃ abrasives remain in both HAp coating and Ti-alloy substrate around the interface. Amorphous phase was not observed at the interface. The grain size of Ti-alloy in the vicinity of the interface is about 10 to 100nm in diameter, while that far from the interface is about 3 μ m in diameter. Miniaturization of Ti-alloy grain around the interface was occurred by plasma spraying. There is no specific crystallographical orientation relationship between HAp and Ti-alloy at the interface, indicating bonding of the interface is essentially mechanical one such as an anchor effect.

Keywords

hydroxyapatite, titanium alloy, interface, orientation relationship, miniaturization of grain, transmission electron microscopy

Introduction

Titanium and titanium alloys are well known as biocompatible materials due to their nontoxic and low elastic modulus. However, since Ti and Ti-alloy will be encapsulated by a fibrous tissue in the body, they cannot directly connect with living bones. This will cause some problems such as fretting wear resulting in inflammation when these alloys are used as bone substitutes or bone repairing materials. Hydroxyapatite (HAp) coating on them, therefore, has been developed, because HAp coating promotes the direct bonding to living bone in the early stage after implantation. There are many methods for HAp coating, e.g., plasma spraying [1-13], RF-sputtering [14-16] and chemical method [17]. Since a plasma spraying is attractive for a high productivity, many biocompatible HAp/Ti-alloy materials in the marketplace have been produced by this method.

There is, however, a problem that HAp coating by plasma spraying is easy to peel-off from Ti-alloy substrate after implantation. It is well known that cohesive of HAp coating is considerably affected by the formation of amorphous phase especially at the HAp/Ti interface [18]. Amorphous phases are frequently formed by the plasma spraying since molten-, or partly molten-particles of coating material with high temperature and velocity impinge the substrate and are rapidly quenched after plasma spraying. There is little study on the microstructures in the vicinity of interface between HAp and Ti-alloy especially by means of transmission electron microscopy (TEM). It is important to analyze the interface structures of HAp/Ti-alloy to understand a peel-off property of HAp coating. In the present study, therefore, the microstructures at/around the interface of HAp/Ti-alloy are analyzed mainly by means of TEM.

Experimental procedures

A cylindrical shape of dental implant, which consists of Ti-alloy with plasma sprayed HAp coating on its surface, was purchased from Sulzer Calcitek Co. Ltd. The cylinder was cut in round slices. Microstructures were

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examined by optical, scanning electron and transmission electron microscopies. The specimens for optical microscopy were polished and etched in the 2.5%HF+2.5%HNO₃+95%H₂O reagent. Thin foils for TEM were prepared by means of a focused ion beam (FIB) HITACHI-FB2000K equipment, and examined in an analytical JEM 2000EX microscope operating at 200kV. X-ray diffractometry was also done to identify their crystal structures of HAp and Ti alloy. The cylinder was split in two for the specimen of X-ray diffractometry. X-ray diffractions were taken from both HAp and Ti-alloy, using Rigaku Miniflex diffractometer, at 30kV and 15mA.

Results

The chemical composition of the Ti-alloy substrate is listed in Table 1. The Ti-alloy is a Ti-6Al-4V alloy containing 0.19wt%Fe and 0.154wt% oxygen. Figures 1(a) and (b) show the X-ray diffractometry results of Ti-alloy substrate and HAp coating, respectively. Ti-alloy has a hexagonal closed packed (hcp) structure denoted by " α -Ti" with solid triangles. On the other hand, coating layer is HAp (solid squares) whose crystallinity is thought to be high since the peaks of HAp in Fig. 1(b) are very sharp. Faint peaks of Al₂O₃ (solid circles) were also detected in Fig. 1(b). Al₂O₃ detected in the study is thought to be an abrasive of blast treatment. Figure 2(a) shows an optical micrograph of Ti-alloy substrate. An average diameter of grains in Ti-alloy is about 3 μ m. Figure 2(b) shows a scanning electron micrograph of cross-section of the HAp/Ti-alloy interface. The interface is winding at an interval of about 100 μ m. Thickness of HAp-coating layer is about 50 μ m. The coating is dense and no crack formation both in the HAp coating and along the interface of HAp/Ti-alloy. TEM micrograph of the microstructure at/around HAp/Ti-alloy interface is shown in Fig. 3. The numbers ①~⑯ in the figure correspond to analyzed areas of composition, and the values obtained are tabulated in the inserted table (at%). Probe size for the composition analysis is about 100nm in diameter. The regions ①~③, ⑥~⑧, ⑪, ⑭ and ⑰ exhibit high content of Al. On the other hand, both Ca and P are rich in the regions of ⑩, ⑫, ⑬ and ⑯. The regions ④, ⑤ and ⑨ contains Ti mainly. Taking into account of the result of X-ray diffractometry, three phases of Al₂O₃, HAp and Ti-alloy exist as indicated by arrows in the figure. It should be mentioned that amorphous phase does not exist between HAp coating and Ti-alloy substrate. Figures 4(a) to (f) show the bright field image, the dark field images taken with $(0\bar{1}\bar{1})_{\text{HAp}}$, $(10\bar{1}1)_{\alpha\text{-Ti}}$ and $(10\bar{1}2)_{\text{Al}_2\text{O}_3}$, the selected area diffraction pattern and the key diagram of (e), respectively. HAp in Fig. 4(b) showing simple net-pattern on the diffraction pattern (f) is large grain, on the other hand, substrate of Ti-alloy consists of fine grains distributing randomly. The diffraction pattern taken from the Ti-alloy grains becomes ring as shown in (f). Therefore, there is no crystallographical relationship between HAp and Ti-alloy. Al₂O₃ has high dislocation density and can be clearly indexed as α -Al₂O₃ as shown in Figs. 4(d) and (f). It should be mentioned that grain size of Ti-alloy in the vicinity of HAp/Ti-alloy interface is quite small, being about several tens nanometer, while that far from the interface is several micrometers in size. Miniaturization of Ti-alloy grains in the vicinity of the interface is induced by plasma spraying. Microstructural change of the Ti-alloy substrate is shown in Fig. 5. The interface of HAp/Ti-alloy exists in the bottom of Fig. 5. The Ti-alloy grains usually contain lattice defects such as dislocations and lath boundaries. Circles with alphabet in Fig. 5 indicate the selected areas for taking diffraction pattern, and the results obtained are shown in Figs. 5(a) to (d). As the selected area is away from the interface, a ring diffraction pattern becomes a spotted pattern. This means grain size of Ti-alloy increases with increasing the distance from the interface. The grain size of Ti-alloy in the area of ④, where it is about 4 μ m away from the interface, is about several hundreds nanometer, and is still much smaller than that in the region thermally-unaffected by spray coating of Ti-alloy.

Discussion

Miniaturization of Ti-alloy grains.

Ti-alloy substrate consists of the α -phase and the grain size is considerably smaller at/around the HAp/Ti-alloy interface than that in the region thermally-unaaffected. It is revealed that the diameter of grain in the vicinity of interface is about several tens nanometer, but is about $3\mu\text{m}$ in the unaffected region. Such the miniaturization of Ti-alloy grain might be induced by heating due to the impingement of molten HAp and a subsequent rapid quenching. At the point of impingement of the molten particles with high temperature and velocity on the substrate, their kinetic energy transforms into thermal and deformation energy. When molten particles impinge the substrate, which is a massive heat sink, they supply their heat to the surface of substrate, cool rapidly and then solidify [19]. It is said that intense heating takes place in the substrate and the thickness of the heat-affected zone attains several tens of microns [19].

There are three possible reasons for realizing such the miniaturization of Ti-alloy grain; (i) rapid quenching of liquid phase, (ii) recrystallization of α -phase, (iii) rapid quenching of β -phase accompanying β - to α -phase martensitic transformation. (i) It is well known that microwelding sometimes occurs at the interface during plasma spraying [19]. Thin layer on surface of Ti-alloy substrate might be melted. However, miniaturization of Ti grains occurred even as far as $4\mu\text{m}$ away from the interface, it is difficult to think all the region, where the miniaturization occurred, was melted. If the regions of $4\mu\text{m}$ from the interface were fully melted, the interface between HAp coating and Ti-alloy substrate should be rougher. Miniaturization of Ti-alloy grains is not due to the rapid quench of liquid phase. (ii) After grit blasting prior to plasma spraying, substrate surface layers have a considerable dislocation density [19]. In the case of the interface being heated above recrystallization temperature, very fine recrystallized α -phase grains would form. Recrystallized grains must have little lattice defects. There is, however, the grains of α -phase around the interface contain high density of dislocations and lath-like structures. Thus, the miniaturization of grains might not be occurred by the recrystallization of α -phase. (iii) If the interface was heated above β -transus temperature, very fine β -phase nucleated on the dense dislocations formed by blast treatment. Subsequent cooling was quite rapid due to the large heat sink of massive Ti-alloy substrate. The rapid quenching would then result in martensitic transformation from β - to α -phase without growing the grain size. It can be concluded that the miniaturization of Ti-alloy grains is caused by the quenching of fine β -phase grains accompanying β - to α -phase martensitic transformation.

Remaining of Al_2O_3 abrasives.

Surface roughening of substrate by blasting with Al_2O_3 abrasives is commonly used to achieve the mechanical anchorage of molten particles into the substrate. Since Al_2O_3 abrasives are hard and brittle, fragments of Al_2O_3 abrasives are frequently embedded in the substrate [2,4]. There is no intermediate phase between embedded Al_2O_3 abrasives and Ti-alloy indicating no reactions occurred during plasma spraying. It can be said that Al_2O_3 abrasives are embedded mechanically in the substrate. In the present study, fragments of Al_2O_3 abrasives exist not only in the substrate but also in the coating layer. Some of Al_2O_3 abrasives, therefore, comes back from the substrate. Al_2O_3 abrasive is probably involved with molten HAp particles during impingement. It should be noted that no reactions could also be detected between Al_2O_3 abrasive and HAp coating. Although the effect of Al_2O_3 abrasives is not clear on the properties of coating, it seems not to degrade the coating property considerably if they are not exposed to external environment. If there were cracks connecting between external environment and Al_2O_3 abrasives through the coating layer, aluminum ions from Al_2O_3 abrasives would be released into the living body, causing a bad effect that an excess of aluminum in contact with bone could inhibit the osteogenic activity of the osteoblast cells [20]. Therefore, remaining Al_2O_3 abrasives should be reduced as possible.

5. Conclusion

Although there is no amorphous phase formation at the interface, there is no specific orientation relationship between HAp and Ti-alloy substrate. The bonding mechanism between the plasma spray HAp coating and the Ti-alloy substrate is fundamentally mechanical anchoring of the HAp to the unevenness surface of Ti-alloy substrate. Therefore, cohesive of HAp coatings is thought to be still poorer. To increase cohesion of HAp coating, chemical bonding should be built at the interface.

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Table 1 Chemical composition of Ti-alloy substrate [mass%].

Al	V	Fe	O	N	Ti
6.35	4.10	0.19	0.154	0.009	bal.

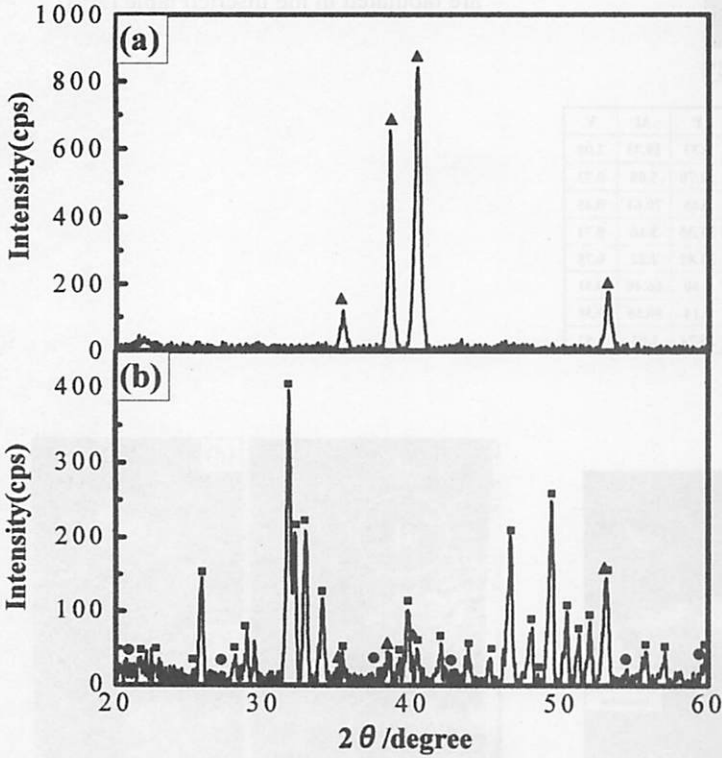


Fig. 1 X-ray diffraction patterns of (a) Ti-alloy substrate and (b) plasma sprayed coating. \blacktriangle α -Ti, \blacksquare HAp, \bullet Al_2O_3 .

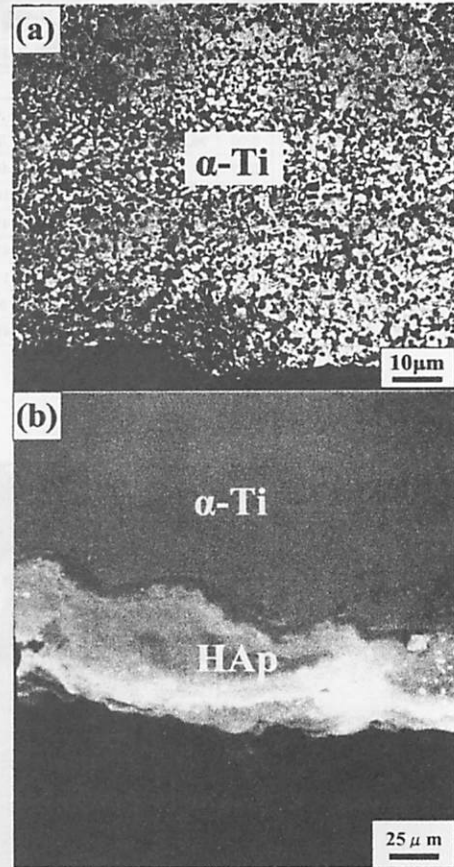
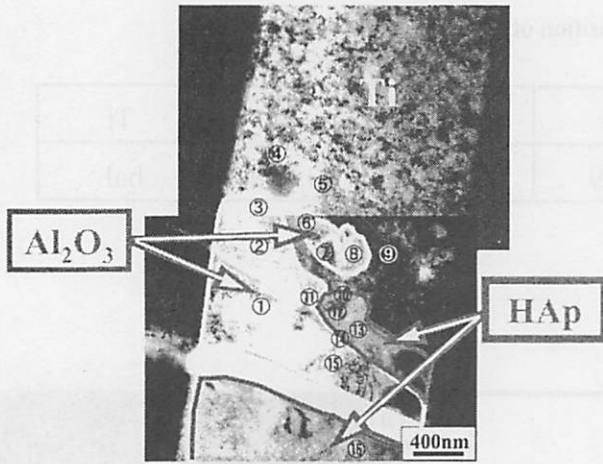


Fig. 2 (a) Optical micrograph and (b) scanning electron micrograph of cross-section of HAp/Ti-alloy.



	Ti	Ca	P	Al	V		Ti	Ca	P	Al	V
①	9.04	0.41	0.00	90.20	0.35	⑨	77.19	0.62	0.37	19.73	2.09
②	11.84	0.26	0.07	87.75	0.08	⑩	16.16	46.33	31.70	5.08	0.73
③	14.51	0.25	0.00	84.67	0.57	⑪	12.69	10.60	5.65	70.61	0.45
④	85.22	0.47	0.23	11.88	2.2	⑫	16.05	48.73	31.35	3.16	0.71
⑤	78.79	0.47	0.34	17.73	2.57	⑬	15.40	49.74	31.89	2.22	0.75
⑥	36.62	1.00	0.10	60.37	1.91	⑭	14.96	11.82	6.50	66.40	0.31
⑦	18.16	0.10	0.17	81.11	0.46	⑮	8.76	0.14	0.14	90.58	0.38
⑧	11.28	0.17	0.02	88.13	0.40	⑯	13.22	48.90	35.74	1.62	0.52

Fig. 3 TEM micrograph of cross-section of HAp/Ti-alloy. The numbers ①~⑯ in the figures correspond to analyzed areas of composition, and the values obtained are tabulated in the inserted table (at%).

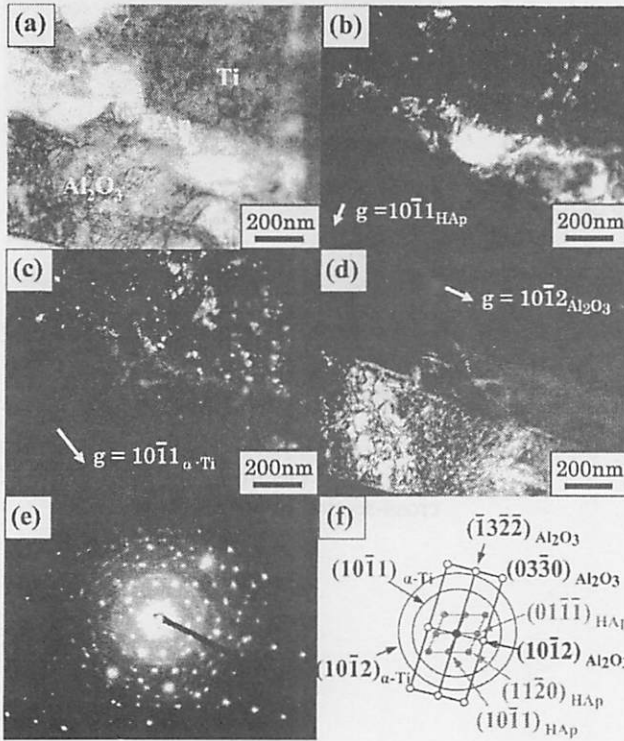


Fig. 4 TEM micrographs at the HAp/Ti-alloy interface: (a) bright field image, (b)-(d) dark field images of $(10\bar{1}1)_{\text{HAP}}$, $(10\bar{1}1)_{\alpha\text{-Ti}}$, $(10\bar{1}2)_{\text{Al}_2\text{O}_3}$, (e) selected area diffraction pattern and (f) key diagram of (e), respectively.

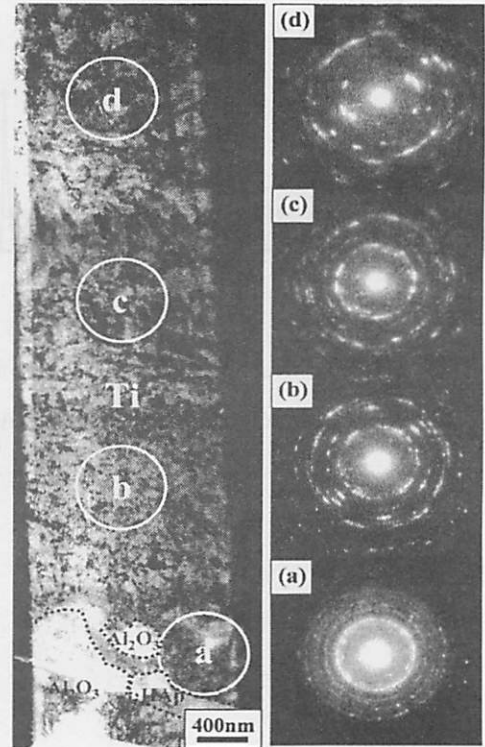


Fig. 5 TEM micrograph of Ti-alloy substrate at/around the interface. The circles with alphabet indicate the areas for selected area diffraction pattern, and the results obtained are shown in (a) to (d).