JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **9** (1998) 643–649

Interfacial characterization of plasma-spray coated calcium phosphate on Ti–6Al–4V

E. PARK, R. A. CONDRATE SR, D. T. HOELZER
New York State College of Ceramics, Alfred University, Alfred, NY 14802, USA
G. S. FISCHMAN
US Food and Drug Administration, Center for Devices and Radiological Health, Rockville, MD 20852, USA

Microstructural characterization was performed on plasma-spray coated calcium phosphate and its interface with Ti–6Al–4V using scanning and transmission electron microscopy. The amorphous calcium phosphate phase was found near the coating/substrate interface, usually in between the crystalline hydroxyapatite grains and the Ti–6Al–4V substrate. The presence of the amorphous calcium phosphate and the channels extending from the interface to the coating surface was attributed to the low interfacial bond strength in a physiological environment. There was an indication of titanium diffusing into the amorphous regions. However, no reaction phases were found between the coating and the Ti–6Al–4V substrate. In the coating area remote from the interface, no intergranular amorphous calcium phosphate phase was observed. The microstructure of the Ti–6Al–4V substrate near the interface was observed to be affected by heat generated during plasma spraying. © *1998 Kluwer Academic Publishers*

1. Introduction

Calcium phosphate coatings, especially plasma-sprayed coatings on metallic substrates, have been developed for the use of medical and dental implants due to their biocompatibility and their ability to bond directly to bone [1]. Biocompatibility of calcium phosphate is based on its chemical resemblance to bone minerals. Mature bone contains 60%–70% calcium phosphate mineral by weight while the remaining fraction is composed of the protein collagen [2]. It has been observed from *in vivo* results that calcium phosphate does not show foreign-body response, such as inflammation and forming an intervening fibrous layer [3]. The direct bone-bonding capability of calcium phosphate is known as osteoconductivity, which means that calcium phosphate allows the direct formation of bone on its surface by acting as a template. The bone-bonding capability of calcium phosphate is also related to the surface porosity. A surface with macropores larger than 100 μm is known to help bone to grow into the structure [4]. Thus by applying a porous coating of hydroxyapatite on metal substrates, usually by a plasma-spray process, one can produce a biocompatible surface that can bond directly to bone. Other advantages of having the coating/substrate assembly include reduced metallic ion release in the physiological environment [5], and better mechanical stability of the assembly due to the tougher nature of metals. Despite these advantages, however, the long-term stability of the plasma-sprayed calcium phosphate on titanium alloy has been questioned, primarily because of the weakness of the coating/substrate interface. In general, the interfacial bond strength between ceramics and metals depends on chemical reactions taking place at the interface. In the case of plasma-spray coated calcium phosphate on titanium alloys, however, it is not clear whether interfacial chemical reactions occur, due to the lack of studies. There have been related studies suggesting the formation of a reaction phase (i.e. Ti–P compound) at the interface between electrophoretically deposited hydroxyapatite and titanium [6, 7]. However, as the coating method was different and the characterization was made on sintered samples, it is difficult to compare their results with a plasma-sprayed system.

The long-term stability of a coating is more important when the influence of a physiological medium is considered. In this case, the stability of coating depends on its dissolution behaviour which can further be related to the amount of amorphous phase present in the coating [8]. The relative amount of amorphous phase in the coating is often referred to as "crystallinity" and is a function of various factors, such as the flame–substrate distance, gas composition (or plasma enthalpy) and the size of starting powder [3]. Amorphous phases are frequently observed from the plasma-sprayed coatings because plasma spraying is a rapid quenching process involving a high temperature. It is believed that the presence and the distribution of the amorphous phase are the key factors that control the long-term stability of the coating.

0957–4530

In this work, plasma-sprayed calcium phosphate coating on Ti–6Al–4V alloy was studied using both scanning (SEM) and transmission electron microscopy (TEM). Efforts were made to correlate the microstructure of the coating and substrate to the interfacial bond strength.

2. Experimental procedure

2.1. Plasma spraying

Fully fired hydroxyapatite was used as starting powder to ensure high crystallinity. The powder consisted of spherical particles in which 94% of the particle size was in the range 53–74 µm. Fig. 1 shows the as-received hydroxyapatite powder. A Ti–6Al–4V alloy was used as the substrate material. The substrate surface was degreased with diluted nitric acid, followed by rinsing with acetone and ethanol. The substrate was then grit blasted with alumina particles to roughen the surface prior to spraying. The parameters used for plasma spraying are listed in Table I.

2.2. Microstructural analysis

After plasma spraying, specimens were examined using both SEM and TEM, along with energy dispersive spectroscopy (EDS). SEM was used for characterization of the coating surface and the fracture surface. For TEM observations, cross-section specimens were prepared by first slicing the specimens into small strips. A sandwich was then made by bonding two strips face to face using a thermosetting epoxy, which was held in a vice to minimize the epoxy thickness, and cured at 70 °C for approximately 4 h. The sandwich was cut down into smaller pieces and embedded in a silver-dispersed epoxy using a specially designed copper mould with 3 mm holes. Embedding was done in such a way that the interface was aligned along the centre-line of a 3 mm hole. The discs were then ground to a thickness of 70–100 µm, and dimpled. The last step involved ion milling, which was followed by coating with an arc-deposited thin layer of carbon. Throughout the sample preparation process, it was found that traditional ion-milling method could not provide sufficient thin area in the interfacial region because of the differential thinning rate between the titanium alloy substrate and the coating. The coating appeared to have a much lower thinning rate than the substrate. Therefore, a Gatan Duomill®, with sector speed control, was used. With sector speed control, it was possible to greatly reduce differential thinning effects by rotating the specimen rapidly as the beam passed along the interface. The specimens were thinned this way at 4 kV with a 12°–15° beam angle. Specimens were examined using a Jeol 2000FX transmission electron microscope operating at 120 kV, equipped with a windowless EDS detector.

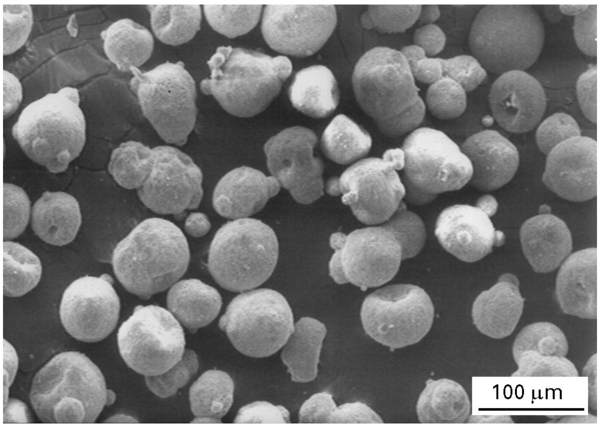

Figure 1 Scanning electron micrograph showing as-received hydroxyapatite powder.

TABLE I Plasma-spraying parameters

Spray gun	METCO Type MBN
Primary gas	Ar
Pressure (p.s.i.)[a]; flow ($ft^3 h^{-1}$)[b]	100; 85
Secondary gas	H_2
Pressure (p.s.i.)[a]; flow ($ft^3 h^{-1}$)[b]	50; 5
Carrier gas	Ar
Flow ($ft^3 h^{-1}$)[b]	37
Powder feed rate ($g\,min^{-1}$)	20
Arc current (A)	400
Spray distance (cm)	10

[a] 10^3 p.s.i. $\simeq$ 6.89 Pa.

[b] 1 $ft^3 h^{-1} \simeq 7.866\ mm^3 s^{-1}$.

3. Results and discussion

3.1. Coating surface

Fig. 2 is a scanning electron micrograph of plasma-sprayed coating surface showing loose particles, splats, pores and cracks. These are typical features in plasma-sprayed coatings. Cracks appeared to be limited to the one or two splat layers near the surface ($\approx$5 µm) because they disappeared as the coating was removed by grinding. These surface cracks could be formed due to thermal expansion mismatch between the coating and the substrate, or to the release of thermal stress generated on cooling. If the former were the case and the hydroxyapatite coating had a higher coefficient of thermal expansion (CTE) than titanium,

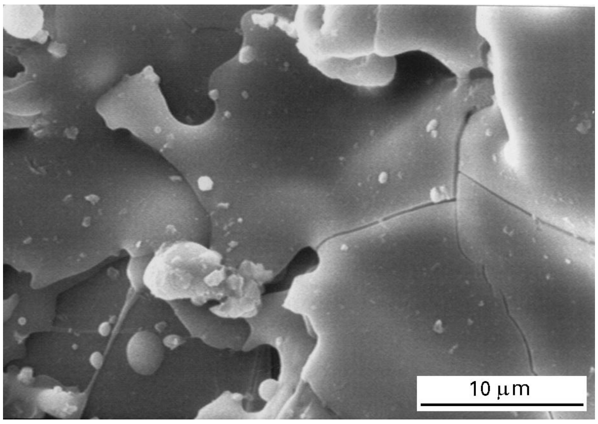

Figure 2 Scanning electron micrograph showing the surface of plasma-spray coated hydroxyapatite.

the coating must have been in tension and the substrate in compression. Then, the coating tends to crack due to tensile stresses built up. Under this situation, cracks should have initiated at the interface and run through the coating thickness. However, such cracks were not observed from a cross-sectional examination of the coating. Therefore, cracks observed in this study were more likely generated by thermal stress that was developed on cooling because the coating surface was cooled more rapidly than the bulk. It is, therefore, important to control carefully the spray parameters in order to reduce surface cracks, because they can lead to the dislodging of poorly adhered particles in a physiological environment. Also, cracks tend to open up in a physiological environment or during post-heat-treatment [9].

3.2. Coating/Ti–6Al–4V interface

It was observed by SEM that when the coating failed, the fracture usually occurred along the calcium phosphate coating/Ti–6Al–4V interface. This observation suggested that a mechanically weak phase existed near the interface. SEM observation of the fracture surface revealed a relatively continuous layer which appeared to be glassy, as seen in Fig. 3. This layer has presumably been formed due to the rapid cooling of the plasma-sprayed powder on to the metal substrate. In the plasma-spraying process, the powder is heated as high as 10 000 °C and then quenched to room temperature in a fraction of a second when it hits the substrate. The high thermal conductivity of the metal substrate initially in contact with the molten powder favours the formation of the amorphous phase under this condition. Close examination of the fracture surface revealed that the amorphous layer was adhered to both sides of the fracture surface. This observation clearly indicates that fracture occurred along the amorphous layer, which acted as the fracture path.

Similar amorphous regions were also observed by TEM (see Fig. 4). The amorphous phase (labelled “A”) was usually found in between the Ti–6Al–4V substrate (labelled “T”) and the crystalline hydroxyapatite grains (labelled “H”). The windowless EDS analysis showed that the amorphous phase consisted of calcium, phosphorus and oxygen, which indicated that this phase was amorphous calcium phosphate (see Fig. 5). In some other amorphous regions, however, EDS showed the presence of titanium in addition to calcium, phosphorus and oxygen. This result suggests the possibility of titanium diffusing into the amorphous calcium phosphate layer. It is possible that a thin layer of calcium phosphate overlaps the Ti–6Al–4V substrate to give a false titanium peak. However, the EDS results were consistent after tilting the specimen stage. The idea of titanium diffusion is also supported by the morphology of the interface between amorphous calcium phosphate and Ti–6Al–4V. The rough interface, as seen in Fig. 4, indicates that mass transport might have occurred. However, no evidence of interfacial reaction was observed. This clearly shows that the bonding mechanism between the plasma-sprayed calcium phosphate coating and the Ti–6Al–4V substrate basically involves mechanical locking of the amorphous calcium phosphate on to the roughened Ti–6Al–4V substrate. However, the formation of reaction phases such as Ti–P compound [6, 7] is also possible if the coating/substrate assembly

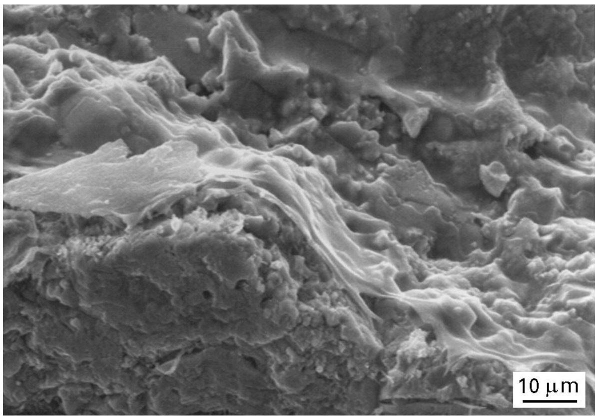

Figure 3 Scanning electron micrograph showing the glassy layer on the fracture surface.

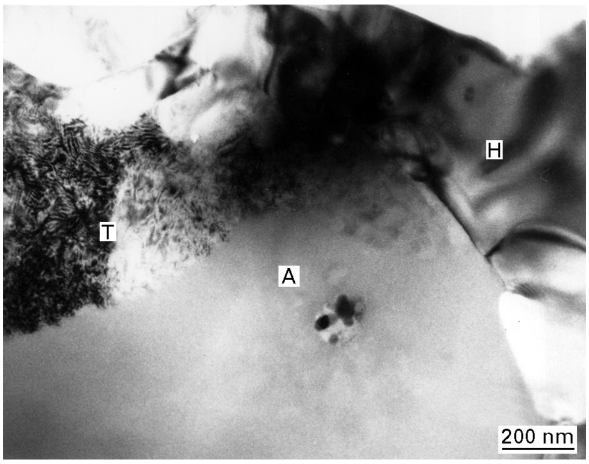

Figure 4 Transmission electron micrograph showing an area near the hydroxyapatite coating/Ti–6Al–4V interface: A, amorphous calcium phosphate; T, Ti–6Al–4V substrate; H, hydroxyapatite.

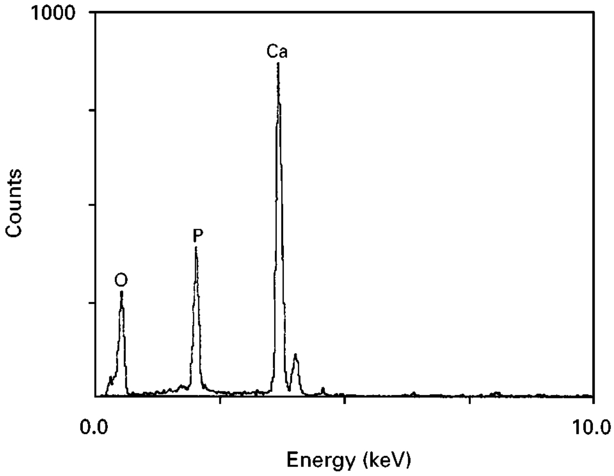

Figure 5 EDS spectra taken from the amorphous region near the interface.

is heat treated, and the compound formation is thermodynamically permitted. Ji *et al.* [10], in working with plasma-sprayed hydroxyapatite on titanium, reported that tricalcium phosphate $(Ca_3PO_4)_2$ and calcium titanate $(Ca_2Ti_2O_5)$ were formed as a result of the reaction between hydroxyapatite and titanium oxide (TiO_2), which was assumed to be present. In our study, however, neither titanium oxide, tricalcium phosphate, nor calcium titanate were found. All selected-area diffraction patterns obtained from the grains near the interface were unambiguously identified as hydroxyapatite. When hydrogen is used as a secondary gas during plasma spraying, it will greatly reduce the formation of titanium oxide. This possibly explains why neither titanium oxide nor calcium titanate were found in the specimen studied in this experiment.

Another feature observed near the interfacial area using SEM was small particles (0.2–1.5 μm diameter) that appeared to be embedded in the glassy material, as shown in Fig. 6a. These particles often contained hollow cores (see Fig. 6b), or consisted of multiple shells between which was filled with glassy materials (see Fig. 6c). A similar observation was also made by TEM as shown in Fig. 7. Grains that were approximately 500 nm diameter appeared to be surrounded by amorphous calcium phosphate. Selected-area diffraction showed that these particles were hydroxyapatite.

The presence of amorphous calcium phosphate phase near the interface was found to be detrimental to the interfacial bond strength, because fracture appeared to occur along the amorphous region. This is more serious when the stability of coating in a physiological environment is considered. Because different phases have different dissolution behaviour, the coating stability depends on the amount of amorphous calcium phosphate phase present. For instance, coatings containing more amorphous phase were found to dissolve much faster in a physiological solution [11]. Yang *et al.* [12] observed over 30% decrease of the interfacial bond strength in a physiological solution over a period of time. Such a large decrease in strength may be due to the preferential dissolution of the amorphous phase at the interface when exposed directly to the solution during the test. Therefore, one should be aware of the interfacial area being exposed to the solution when the coating/substrate assembly is subjected to mechanical tests in a physiological solution, because fast dissolution of the amorphous phase will degrade the interfacial bond strength. Even when the interfacial area is covered by the coating, as in the case of a cylindrical implant, the area may still be exposed to the physiological environment if the coating is porous. In highly porous coatings, voids can be interconnected three-dimensionally and form channels. It was observed in the cross-sectional examination of the coating that channels or interconnected voids extending from the coating surface to the interface were present (see Fig. 8). These channels were often observed in thin, highly crystalline, and porous coatings. The presence of such channels is important because the amorphous phase near the interface and the metal substrate can be exposed to the physiological environment. This will decrease the interfacial bond strength and cause metal elements to be leached into the physiological medium. It is thus essential to make the coating dense in order to protect the interfacial area from the physiological solution. On the other hand, however, a macroporous coating surface is required to improve bonding with tissue. Therefore, the coating needs to be designed in such a way that the surface is porous but the area near the interface is dense.

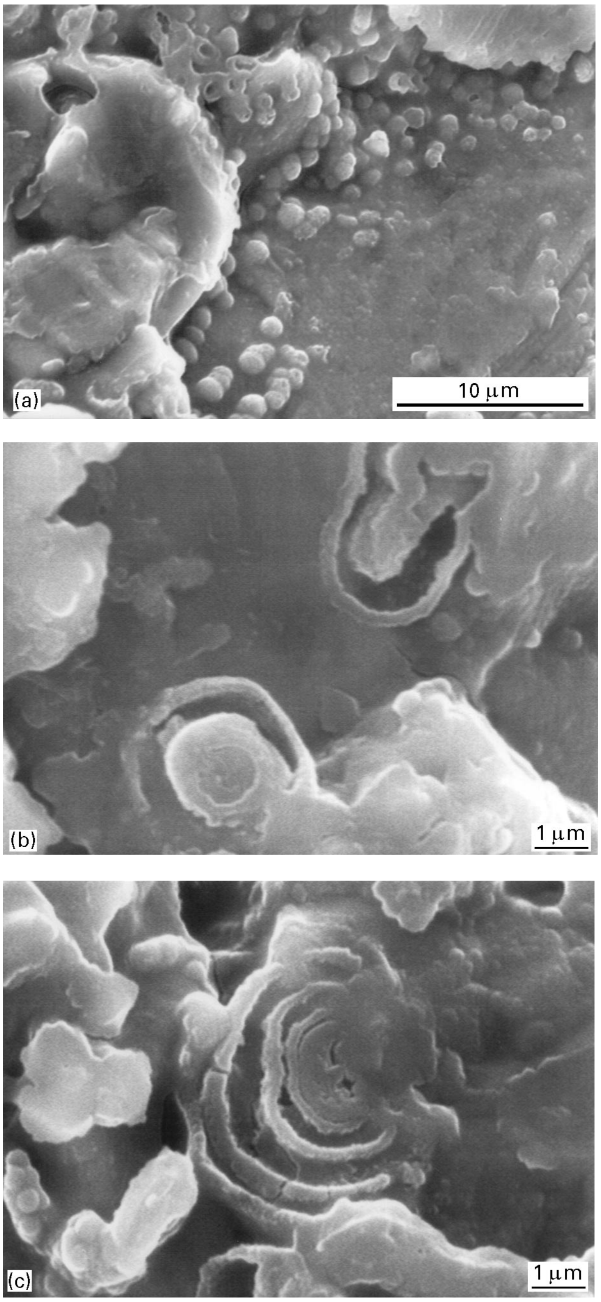

Figure 6 Scanning electron micrograph showing (a) embedded particles in the glassy material on the fracture surface of plasma-spray coated hydroxyapatite. The particles contain (b) hollow cores and (c) multiple shells.

3.3. Bulk coating

In the area immediately adjacent to the amorphous calcium phosphate phase, crystalline hydroxyapatite

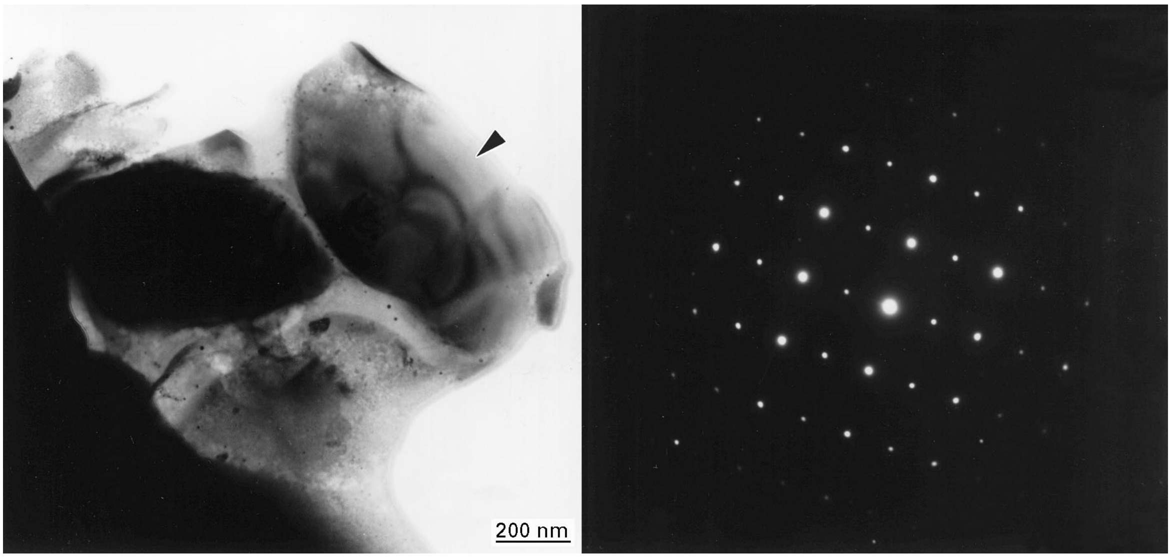

Figure 7 Transmission electron micrograph showing hydroxyapatite particles embedded in amorphous calcium phosphate.

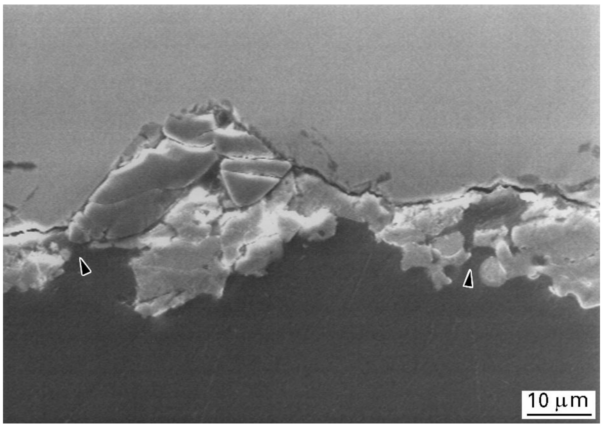

Figure 8 Scanning electron micrograph showing channels (marked arrows).

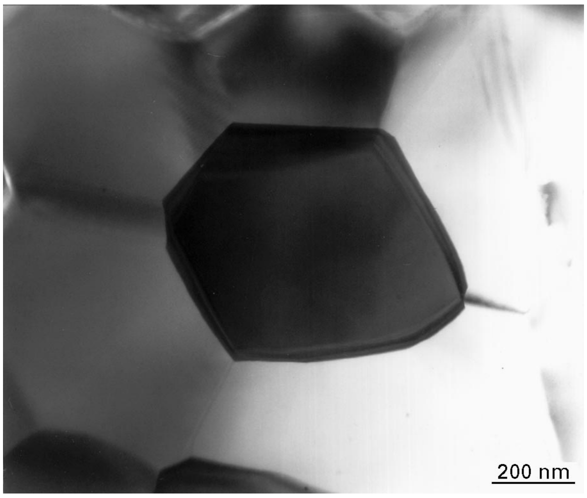

Figure 9 Transmission electron micrograph showing hydroxyapatite grains in the area remote from the interface.

grains were observed as shown in Fig. 4 (labelled "H"). These grains were relatively small (≈ 200 nm) and appeared to have been formed by crystallization from the amorphous calcium phosphate during cooling. In the bulk of the coating remote from the interface, large equiaxed hydroxyapatite grains were observed as shown in Fig. 9. There was no intergranular amorphous phase found in this area. The size of these grains (≈ 700 nm) was more than three times larger than those observed near the interface. The grain-size difference is presumably due to different cooling rates between the bulk and interface regions. The finer grains were formed near the metal substrate which acted as a heat sink and led to the higher cooling rate.

3.4. Effect of alumina particles (roughening medium)

Roughening the substrate surface using ceramic abrasives, such as alumina or silicon carbide, is commonly employed as a way to improve the coating–substrate bond strength. This improves the interfacial bond strength, because molten splats are mechanically locked on to the roughened surface better than the smooth surface. However, it was frequently observed that alumina particles used as ceramic abrasives were embedded in the Ti–6Al–4V substrate as seen in the scanning electron micrograph (Fig. 10). The interface between the alumina and the Ti–6Al–4V substrate appeared to be clean, which indicated that no reactions had taken place. This is probably because the roughening process does not involve external heat other than heat generated by friction. Although the effect of ceramic abrasives embedded in the titanium alloy substrate is not clear, it does not appear to degrade the integrity of the coating. However, some abrasive particles were observed to have cracks that were possibly produced by high-velocity impact. These cracks will decrease the interfacial bond strength.

3.5. Ti–6Al–4V substrate

The microstructure of the Ti–6Al–4V substrate was also studied using TEM. The analysis showed that the

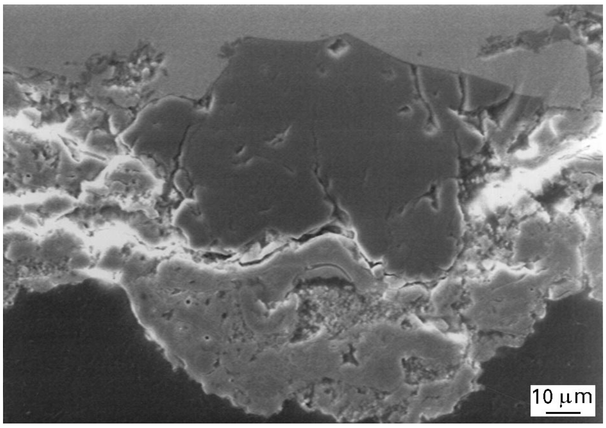

Figure 10 Scanning electron micrograph showing an alumina particle embedded in the Ti–6Al–4V substrate.

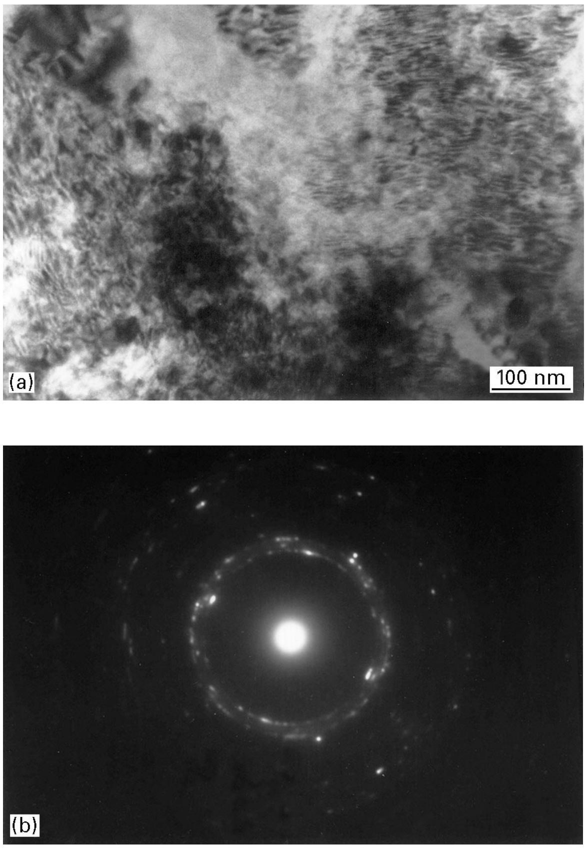

Figure 11 Transmission electron micrograph of the area immediately adjacent to the interface, showing (a) fine-grained Ti–6Al–4V and (b) selected-area diffraction pattern.

substrate consisted of the α-HCP phase and that the grain size was smaller near the coating/substrate interface than in the bulk region. It was found that the grain size near the interface was ≈20 nm, which is shown in Fig. 11a, but was typically up to ≈5 μm in the bulk region. The selected-area diffraction pattern (see Fig. 11b) obtained near the interface shows nearly continuous rings. This result is consistent with a small grain size and a random grain orientation of the α-phase in this region. This result also indicates that the microstructure has been altered near the coating/substrate interface by the plasma-spraying process.

The results, showing a decrease in the grain size of the α-phase, indicate that the temperature near coating/substrate interface was increased to above the β-transus temperature. The heat that caused this temperature increase was supplied by the molten splats during the plasma-spraying process. It is suggested that the subsequent cooling rate was rapid due to the large heat-transfer properties of the metallic substrate. The faster cooling rate would then result in the refinement of the grain size for the α-phase during the β to α solid-state phase transformation. Furthermore, it is believed that a thin layer of the metallic substrate was melted from this rise in temperature because the molten state could facilitate the rapid diffusion of titanium into the amorphous calcium phosphate phase, which was previously discussed.

4. Conclusion

Characterization of the interface between plasma-sprayed calcium phosphate coating and Ti–6Al–4V was performed by using SEM and TEM along with EDS. Cracks were found to be limited to the area near the surface, and were presumably formed due to release of thermal stress generated on cooling.

The amorphous calcium phosphate phase was found at the interface. This phase was formed due to the rapid-quenching nature of the plasma-spraying process. Examination of the fracture surface indicated that this amorphous phase acted as a fracture path. The presence of amorphous phase and channels was related to the decrease of interfacial strength in a physiological environment. TEM analysis showed evidence of titanium diffusing into the amorphous calcium phosphate region; however, no evidence of reaction phases was found at the interface. This indicates that the interfacial bonding in the as-sprayed (not heat-treated) sample involves basically mechanical locking of molten splats on to the roughened substrate surface.

The alumina particles used for roughening the substrate surface were observed to be embedded in the substrate. Unless these particles contain cracks, they do not appear to degrade the interfacial bond strength. The microstructure of Ti–6Al–4V near the interface showed that the area has been affected by the heat generated during plasma spraying. The heat treatment after spraying may further alter the microstructure of the substrate.

Acknowledgement

This work was supported by the Center for Advanced Ceramic Technology and Industry University Center for Biosurfaces at Alfred University.

References

1. M. JARCHO, *Clin. Ortho. Rel. Res.* **157** (1981) 259.
2. A. S. POSNER, N. C. BLUMENTHAL and F. BETTS, in "Proceedings of the 2nd International Conference on Phosphorous Compounds", edited by C. Eon (IMPHOS, Paris, 1980) p. 25.

3. C. P. A. T. KLEIN, J. G. C. WOLKE and K. DE GROOT, in "An Introduction to Bioceramics", edited by L. L. Hench and J. Wilson (World Scientific, Singapore, 1993) p. 199.
4. J. J. KLAWITTER Jr, PhD thesis, Clemson University (1970).
5. P. DUCHEYNE and K. HEALY, *J. Biomed. Mater. Res.* **2** (1988) 1137.
6. W. VAN RAEMDONCK, P. DUCHEYNE and P. DE MEESTER, *J. Am. Ceram. Soc.* **67** (1984) 381.
7. P. DUCHEYNE, W. VAN RAEMDONCK, J. C. HEUGHERBAERT and M. HEUGHERBAERT, *Biomaterials* **7** (1986) 97.
8. M. WEINLAENDER, J. BEUMER III, E. B. KENNEY, P. K. MOY and F. ADAR, *J. Mater. Sci. Mater. Med.* **3** (1992) 397.
9. K. A. GROSS and C. C. BERNDT, in "Characterization and Performance of Calcium Phosphate Coatings for Implants", edited by E. Horowitz and J. E. Part (ASTM, Philadelphia, PA, 1994) p. 124.
10. H. JI, C. B. PONTON and P. M. MARQUIS, *J. Mater. Sci. Mater. Med.* **3** (1992) 283.
11. C. P. A. T. KLEIN, J. M. A. DE BLIECK-HOGERVORST, J. G. C. WOLKE and K. DE GROOT, in "Ceramics in Substitutive and Reconstructive Surgery", edited by P. Vincenzini (Elsevier, The Netherlands, 1991) p. 363.
12. C. Y. YANG, B. C. WANG, E. CHANGE and B. C. WU, *J. Mater. Sci. Mater. Med.* **6** (1995) 258.

Received 15 April
and accepted 25 September 1997