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Microstructural characterization of hydroxyapatite coating on titanium

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The microstructure of hydroxyapatite plasma sprayed onto titanium alloy has been studied by using transmission electron microscopy. It has been shown that while substantial portions of the coating are crystalline hydroxyapatite, regions of amorphous calcium phosphate with Ca/P ratios of 0.6–1.0 are also present, both in the coatings and at the metal–ceramic interface. The microstructures observed have also been found to be consistent with devitrification of the amorphous calcium phosphates producing regions of very fine grained hydroxyapatite. A calcium titanate phase has also been detected at the metal–ceramic interface produced by the chemical reaction of hydroxyapatite to titanium.

1. Introduction

Hydroxyapatite is well established as a biocompatible ceramic capable of forming a good bond with natural bone [1]. The principal limitation in the clinical use of hydroxyapatite as a load-bearing implant is mechanical brittleness. Although metal implants have superior mechanical properties, concern over the toxic responses continues to increase. There has therefore been significant recent interest in the use of hydroxyapatite-coated metal implants which it is believed accelerate the rate of bone bonding and act as a biological barrier between the body and the metallic parts of the system. Plasma-sprayed hydroxyapatite coatings provide a surface macrotexturing which following bone growth can generate enhanced mechanical keying of bone to implant. Hydroxyapatite-coated titanium implants have been found to have significantly greater interfacial shear strength, measured by using mechanical push out tests [2]. However, the long-term stability of the coatings depends on a number of factors, including the microstructure and range of the calcium phosphate phases produced during the plasma-spraying process. Energy dispersive X-ray studies have revealed interfacial layers, containing titanium and phosphorous [3], which have a distinctively different composition from the top coatings. The level of solubility of the different calcium phosphate phases that can be produced during plasma spraying can vary by as much as an order of magnitude. However, it is not very clear from previous studies how the plasma-spraying process alters the crystallography of the hydroxyapatite which is sprayed and therefore changes the bioactivity and lifetime of the coating. This paper reports the results of an interfacial characterization of a plasma-sprayed hydroxyapatite coating using both scanning and transmission electron microscopy.

2. Experimental procedure

The surface of 20 mm diameter titanium alloy test buttons was blasted with 20 mesh alumina and degreased. Hydroxyapatite powder with a particle size of 45–115 μm was coated onto the prepared titanium alloy buttons by using a plasma-spraying deposition process at 65 V and 450 A, producing a coating 200 μm thick. The carrier gas used in the spraying process was argon.

The nature of the resulting coating was determined by using X-ray diffraction with CuK_α radiation. A cross-sectioned specimen of the calcium phosphate coating on the titanium was cut from the test button with a diamond saw and polished on a Multipol 2 polisher with syton at the grade of 0.1 μm for the examination by scanning electron microscopy. Transmission electron microscopy specimens were prepared from the cross-sectioned samples by using a dimpler and ion-beam thinning, and subsequently examined in a Philips EM400T and JEOL 4000FX at 100 kV and 400 kV, equipped with energy dispersive X-ray analysis detector.

3. Results and discussion

The coating of titanium implants should in principle combine the mechanical and bioinert properties of a well-established implant metal with the osteoconductive properties of hydroxyapatite. A typical X-ray diffraction pattern obtained from the surface of the coating obtained in the current study is shown in Fig. 1. The X-ray diffraction pattern of the coating matches the standard diffraction pattern for pure hydroxyapatite. However, there is evidence of traces of α-tricalcium phosphate (α-$Ca_3(PO_4)_2$) in the hydroxyapatite coating as indicated by the arrow in Fig. 1.

A scanning electron micrograph taken from a cross-sectioned sample of the plasma-sprayed hydroxyapatite coating on the titanium is shown in Fig. 2. It can be seen that the coating is built up of layers of flattened particles. During the plasma-spraying process the hydroxyapatite particles are injected into an

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argon gas system and carried into a plasma flame which totally melt or soften the surface of the particles. When these particles impact on the substrate at velocity, they become flattened and adhere to the surface by mechanical interlocking. The laminated structure produced is typical of plasma-spraying coating [4].

The transmission electron microscopy studies revealed the presence of a range of phases the crystal form of which was established by using electron diffraction. In Fig. 3 a typical region of amorphous calcium phosphate adjacent to crystalline hydroxyapatite is shown. The results of the energy dispersive analysis (EDX) on both phases showed that the relative ratio of Ca to P in the crystalline phase is approximately 1.5 compared to a Ca/P ratio about 0.8 in the amorphous phase. Amorphous regions were detected throughout the hydroxyapatite coating resulting in significant variations in the Ca/P ratios in the coating [5]. It is well known that for most plasma flame spraying processes temperatures in the 6600–11 000 °C range can be obtained. As a result during plasma spraying, the hydroxyapatite powder may be totally or partly melted. When the melted hydroxyapatite particles are coated onto the metallic substrate they can either crystallize or form amorphous calcium phosphates. During the rapid cooling that occurs as the particle impact on the surface compositional changes can also occur as both phosphate and calcium ions migrate. In addition it is possible that as the amorphous phase cools it may fully or partly crystallize. However, in the case of plasma spraying, the extent of crystallization may be limited because of the rapid cooling produced as the heated powder impacts on the relatively cooler surface. A considerable amount of the coating is therefore likely to be deposited in the amorphous glass phases [6]. Fig. 4a shows the crystalline phase in an amorphous matrix in the hydroxyapatite coating. Selected area diffraction patterns taken from the crystalline and amorphous phases are shown in Fig. 4b and c respectively. The diffraction pattern from the crystalline phase shows a series of rings, associated with the size and magnitude of the crystalline grains. By contrast the pattern from the amorphous matrix has a diffuse ring pattern. Crystalline grains in the amorphous matrix will either have been produced by crystallization of the amorphous phase or are residual crystalline material resulting from a lack of total melting in the sprayed crystalline powder.

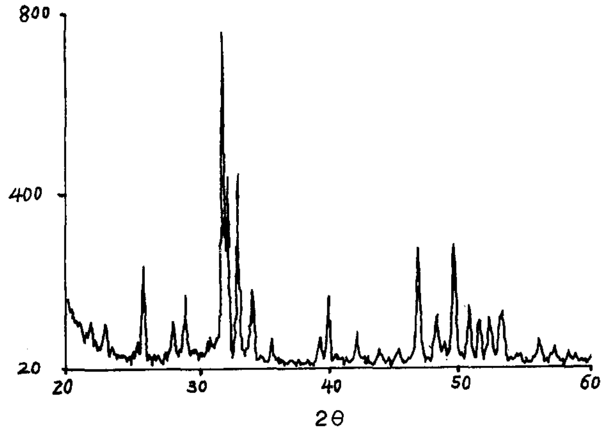

Figure 1 X-ray diffraction trace taken from the surface of a plasma-sprayed hydroxyapatite coating on titanium.

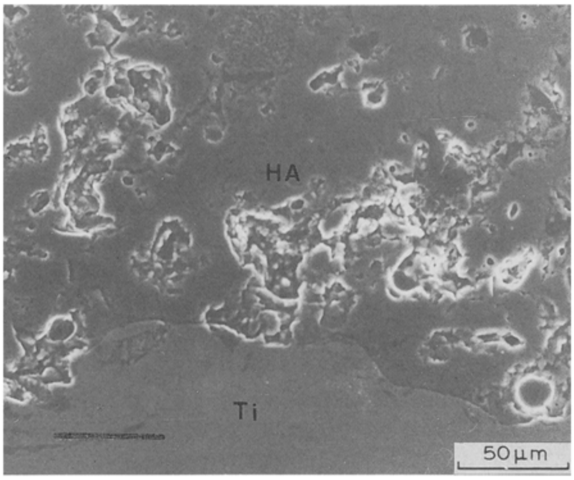

Figure 2 SEM micrograph taken from a cross-sectioned sample of plasma-sprayed hydroxyapatite coating on the titanium: (HA) hydroxyapatite, (Ti) titanium.

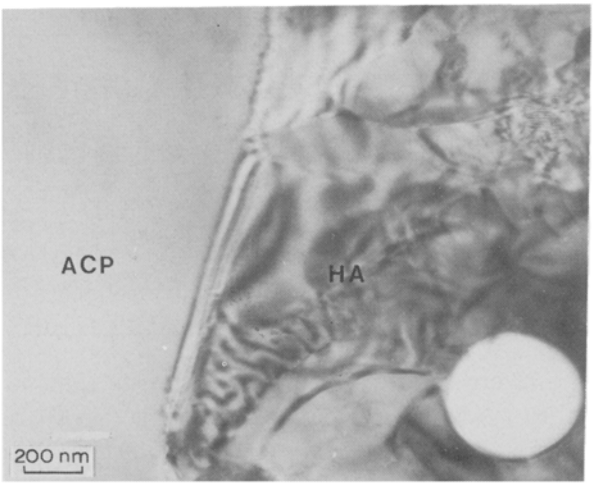

Figure 3 TEM micrograph taken from hydroxyapatite coating showing both crystalline and amorphous phases: (HA) crystalline hydroxyapatite, (ACP) amorphous calcium phosphate.

Different grain sizes of crystalline hydroxyapatite were also observed at different points in the coating. Close to the titanium substrate hydroxyapatite grain sizes around 100 nm were observed as shown in Fig. 5a. Further from the metal interface larger 500 nm grains were present as illustrated by the micrograph shown in Fig. 5b. The presence of the fine 100 nm grains indicates that the formation of the fine grains of hydroxyapatite may be caused by the recrystallization of the amorphous phase. In the interior of the coating the hydroxyapatite grain size showed little variation. To determine the crystal system from the selected area diffraction patterns taken from hydroxyapatite coating, we can get the measured values of interplanar angles, *d*-spacings, and angles of tilt between the electron beam directions. Then theoretical calculation

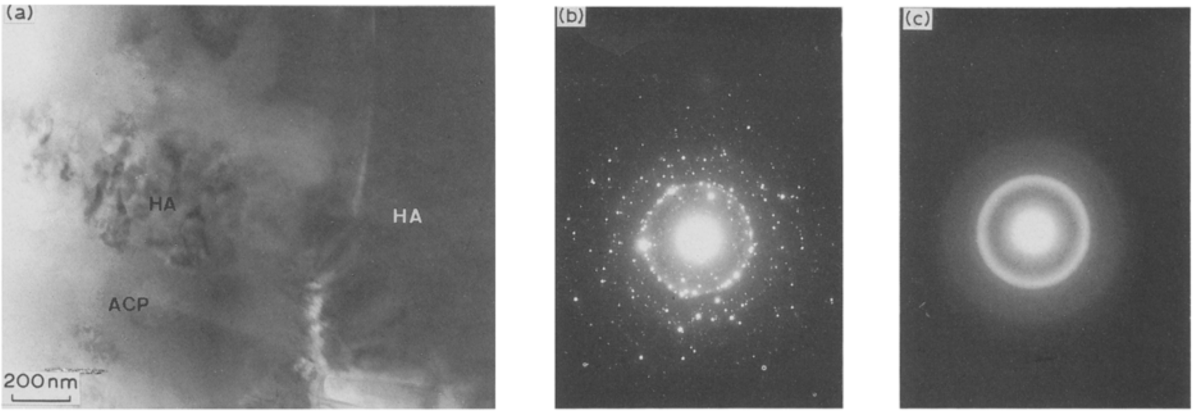

Figure 4 (a) TEM micrograph taken from hydroxyapatite coating shows crystalline phases within the amorphous phase. (b) A selected area diffraction pattern from the crystalline phase showing a ring pattern consistent with a polycrystalline structure. (c) A selected area diffraction pattern taken showing diffuse rings from the amorphous phase. (HA) Crystalline hydroxyapatite, (ACP) amorphous calcium phosphate.

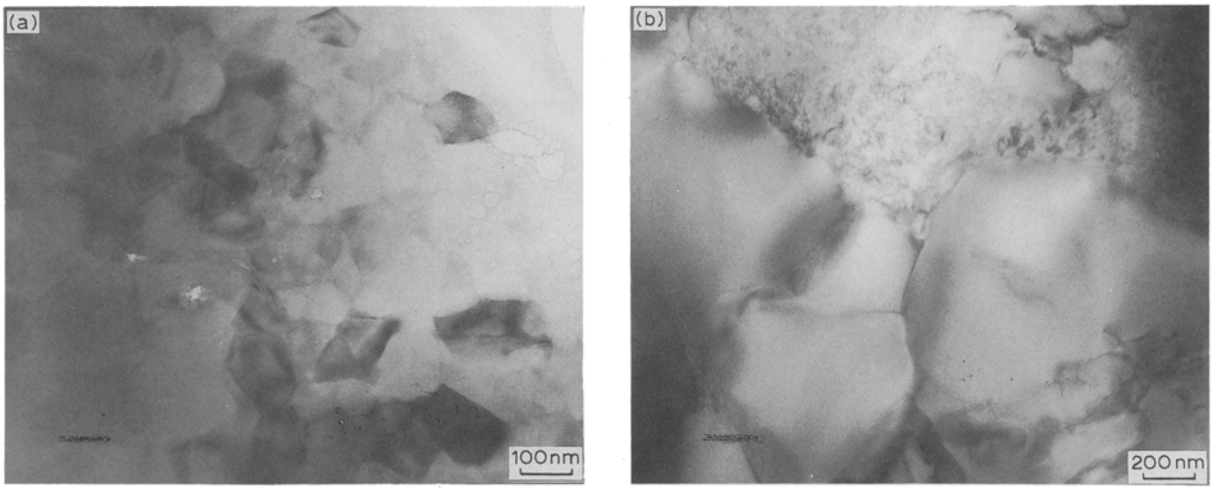

Figure 5 TEM micrographs showing fine grains of crystalline hydroxyapatite (a) from regions close to the metal interface and the larger grains of crystalline hydroxyapatite (b) in the bulk of the coating.

values based on the assumption according to EDX results from the observed area are compared with these measured values. Hence, the determination of the crystal system is based on the theoretical values close to the measured values. Several electron diffraction patterns were analysed from a series of positions in the coating and Fig. 6 shows typical selected area diffraction patterns. These diffraction patterns are very closely indexed to the hydroxyapatite structure ($Ca_{10}(PO_4)_6(OH)_2$). However, it is found from indexing all of the diffraction patterns taken from the hydroxyapatite coating that most of the diffraction patterns are nominally α-tricalcium phosphate (α-$Ca_3(PO_4)_2$). The apparent conflict between the electron diffraction data and the X-ray diffraction results can be explained by the fact that during examination by TEM in high vacuum, the release of hydrogen may cause the conversion of hydroxyapatite to α-tricalcium phosphate structure [7]. Further confirmation that the bulk of the coating comprises of hydroxyapatite is provided by the Ca to P ratios in the coating which were determined to be in the range 1.5–1.8, compared to 1.67 for hydroxyapatite.

A TEM micrograph of the interface between hydroxyapatite and titanium is shown in Fig. 7. The coating adjacent to the interface is an amorphous phase with a Ca to P ratio of about 0.7. It is interesting to see crystalline phases in the amorphous phase in addition to a good bonding between the coating and titanium. In the case of the amorphous phase with its high phosphorous content at the interface there could be a tendency to form titanium phosphorous compounds as phosphate ions diffuse into the titanium and the amorphous phase is transformed into the crystalline calcium phosphate with a lower phosphorous content. Some chemical bonding could then be generated at the interface although the majority of the bonding is likely to remain the mechanical interlocking produced by the plasma-spraying process. Under reducing or at minimum non-oxidizing condition, phosphate ions will diffuse into the titanium to form a titanium phosphorous compound and leave a residual calcium phosphate. Alternatively under oxidizing conditions the hydroxyapatite would be transformed to tricalcium phosphate as the titanium oxide produced removes calcium ions through the forma-

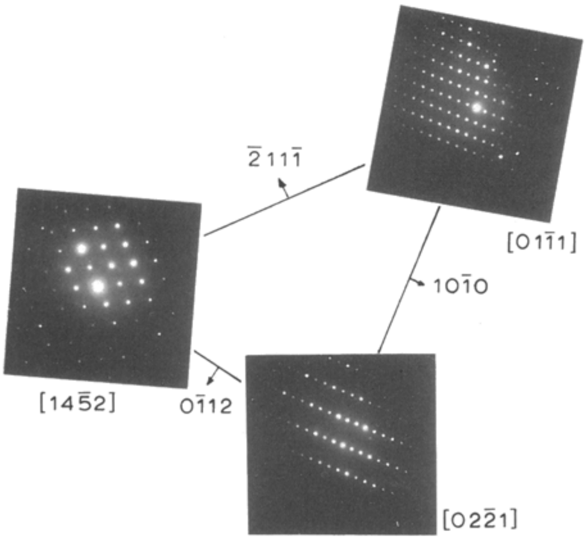

Figure 6 Selected area diffraction patterns taken from the coating indicating the presence of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) with the hexagonal lattice parameters: $a = 0.9148$ nm and $c = 0.6884$ nm.

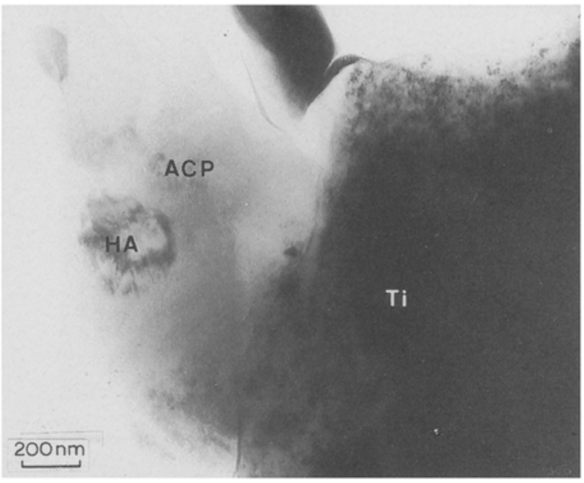

Figure 7 TEM micrograph showing the interface between amorphous calcium phosphate and the titanium substrate: (HA) crystalline hydroxyapatite, (ACP) amorphous calcium phosphate, (Ti) titanium.

tion of calcium titanium oxide ($CaTi_2O_5$) as shown in the following reaction:

$$(n+1)Ca_{10}(PO_4)_6(OH)_2 + 2nTiO_2 \rightarrow (n-1)Ca_{10}(PO_4)_6(OH)_2 + 3nCa_3(PO_4)_2 + nCaTi_2O_5 + 2H_2O \quad (1)$$

The tricalcium phosphate can exist in two crystalline forms, a high-temperature form, α-$Ca_3(PO_4)_2$ and a low-temperature form, β-$Ca_3(PO_4)_2$ [8]. In the case of plasma spraying it is probable that the α-tricalcium phosphate (α-$Ca_3(PO_4)_2$) will be formed. A typical TEM micrograph of substrate coating interface is shown in Fig. 8a. It is known that the titanium alloy used as the substrate in the current study was an alpha alloy with the hexagonal lattice parameters; $a = 0.29511$ nm and $c = 0.46843$ nm, but included an additional beta alloy with the cubic lattice parameter; $a = 0.33065$ nm. Selected area diffraction patterns taken from the substrate just adjacent to the coating have been indexed to $CaTi_2O_5$ with the lattice parameters, $a = 1.292$ nm, $b = 0.990$ nm and $c = 1.604$ nm, and the orthorhombic structure (see Fig. 8b). The results of indexing diffraction patterns from the coating indicate that the crystalline calcium phosphate phase is α-$Ca_3(PO_4)_2$ (see Fig. 8c). These results are clearly consistent with the reactions described above.

The microstructural observations reported in this paper clearly demonstrate that a plasma-sprayed hydroxyapatite coating is likely to contain both a number of calcium phosphate phases in addition to variations in the grain size and degree of crystallinity of the hydroxyapatite regions. A major concern about the use of plasma-sprayed hydroxyapatite coatings is their long-term stability in the body. The coatings studied in this paper would be likely to have very varied solubility since the extra grain boundary area of the fine grained regions would enhance dissolution rates and the different calcium phosphate phases ob-

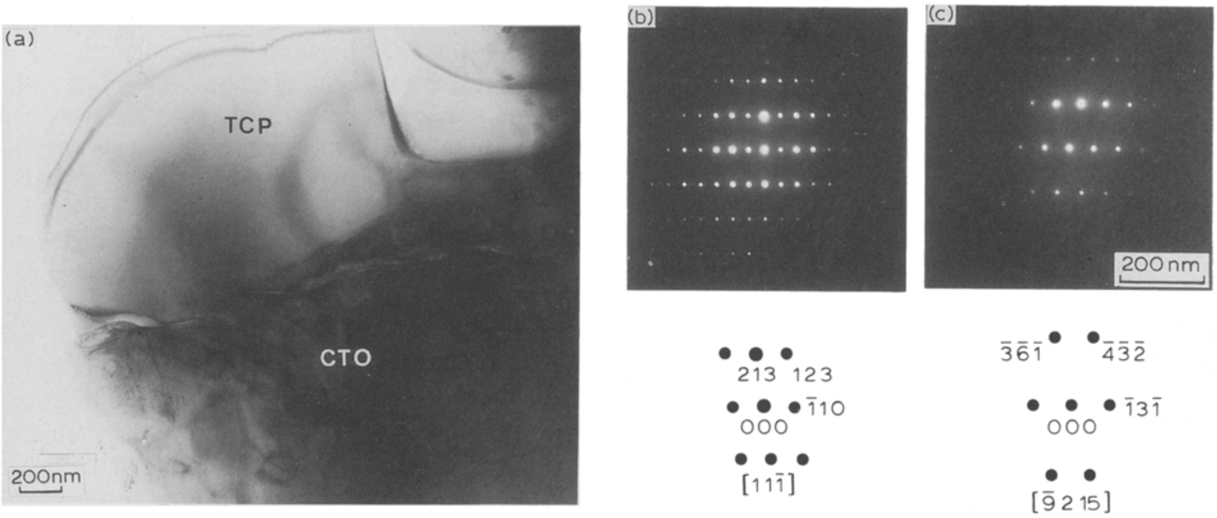

Figure 8 (a) TEM micrograph showing the interface between tricalcium phosphate and calcium titanium oxide. (b) A selected area diffraction pattern from calcium titanium oxide, indexed to $CaTi_2O_5$ in the pole of $[1\,1\,\bar{1}]$. (c) A selected area diffraction pattern from tricalcium phosphate indexed to α-$Ca_3(PO_4)_2$ in the pole of $[\bar{9}\,2\,15]$. (CTO) $CaTi_2O_5$, (TCP) α-$Ca_3(PO_4)_2$.

served are known to have different rates of solution. Given that the microstructure of a plasma-sprayed coating will be dependent on the processing parameters it is apparent that great care must be exercised when comparing the performance of coatings prepared by different manufacturers using different conditions and source of hydroxyapatite powders.

4. Conclusion

Good adhesion of hydroxyapatite coatings to titanium can be obtained by using plasma spraying; some chemical bonding occurs at the interface in addition to mechanical interlocking. The chemical products produced at the interface by this interaction are α-$Ca_3(PO_4)_2$ and $CaTi_2O_5$. In addition during the deposition of hydroxyapatite by plasma spraying, the crystalline hydroxyapatite appears to be produced combined with an amorphous glass phase of calcium phosphate, particularly at the interface. These regions of amorphous calcium phosphate have a low calcium to phosphorous ratio of 0.6–1.0 and show evidence of partial recrystallization.

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