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Raman microprobe investigation of the calcium phosphate phases of three commercially available plasma-flame-sprayed hydroxyapatite-coated dental implants

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The purpose of the current study was to evaluate the crystallographic properties of three commercially plasma-flame-sprayed hydroxyapatite (HAp) coatings on dental implants. For this purpose a Raman microprobe (MOLE U1000) was used. No preparation of the surfaces was necessary to examine the thin ceramic surface layers. Microspectra (5 μm) and macrospectra (100 μm) have been measured and compared to the spectra of crystalline and amorphous HAp as well as to the spectra of tricalciumphosphate. All implants showed spectra that were more like that of the amorphous phase of HAp than any of the other examined reference materials. However, the implant spectra exhibited an extra band that as yet has not been identified. This band is probably indicative of some structure within the sprayed amorphous phase. Such structural effects would result either directly from quenching from the plasma state or by incorporation of titanium into the lattice during plasma treatment.

1. Introduction

Calcium phosphate biomaterials have been studied for use as bone substitutes for more than a decade [1–12]. The interest in calcium phosphate ceramics (CPCs) for medical and dental applications is derived from the absence of toxic components and their resemblance to the inorganic phase of the human skeleton. One of the most outstanding features of CPCs is their apparent ability to become directly bonded to bone. At the interfaces of CPC implants, bone is usually found to be deposited directly on the implant surface without an intervening fibrous tissue layer [28]. Because CPCs are composed of the same ions as bone mineral, these ceramics are capable of participating in solid–solution equilibrium interactions at their surfaces. The required ions to establish these equilibria may be derived from the implant, the surrounding bone, or both. It is to be expected that the composition of any solids deposited at these implants would largely be determined by the surrounding physiological media, i.e. biological apatite [6]. Among the more recent bioceramics used as bone substitutes are hydroxyapatite (HAp, $Ca_{10}(PO_4)_6OH_2$) and tricalciumphosphate (TCP, $Ca_3(PO_4)_2$). The principal limitation in the use of CPCs as dental implants is derived from their mechanical brittleness. Ceramics are characteristically stronger in compression than in tension but brittleness makes them mechanically inferior to bone and metal. They are useful only in applications where the forces are compressive. The combination of the superior mechanical properties of a metallic base such as titanium with a CPC coating can overcome the mechanical problems while maintaining the biological and osteophilic properties [14–19]. This has been the basis for using CPC-coated titanium implants.

One method for applying the CPC coating utilizes the plasma flame spray technique. In this process pulverized HAp particles (50–100 μm) are injected into an argon gas stream and carried into a plasma flame whose temperature is between 15 000 and 20 000 °C. Very small particles ($<$ 5 μm) may melt and vaporize before impact on the substrate. Particles that are too large to melt (100 μm) will actually fall out of the flame due to gravitational effects or rebound from the substrate. Those particles which are able to melt partly or completely become incorporated in the deposit. The thickness of these coatings can be made from 30 μm to several millimetres of thickness [20]. Current HAp-coated dental implants have a coating thickness of about 0.03–0.04 mm. The plasma flame spray technique results in a ceramic coating which is more strain resistant and which has improved mechanical properties when compared to other ceramics formed by a sintering process [20].

However, it is possible that the plasma flame spraying process alters the crystallographic properties of HAp, which might change the bioactivity of the ceramic coating. To achieve a biostable coating on

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these implants the coating has to be of a high crystallinity and be consistent with the ASTM F4 Committee (American Society for Testing Materials, Philadelphia, PA) powder diffraction file for HAp.

2. Materials and methods

The present study was initiated to examine the crystallographic properties of plasma-flame-sprayed ceramic coatings of three commercially available dental implants. Since X-ray diffraction or infrared absorption require a certain amount of material for identification and Auger and electron microprobes are incapable of yielding chemical or crystallographic identification, it was decided to use the Raman microprobe (RMP) MOLE U1000 (Molecular Optical Laser Examiner).

Raman spectroscopy is a light scattering phenomenon identified in 1928 where monochromatic laser photons are scattered by molecular and crystalline vibrations of a sample. The resulting photons have lower energy and therefore appear at wavelengths longer than that of the exciting laser. Raman spectra can be used to identify molecular components and crystal structures [21]. The RMP requires sample preparation identical to that for optical microscopy, has spatial resolution as good as 1 μm, and is used for fingerprint identification of microscopic contaminants, inclusions and films and for the characterization of technologically important new materials.

One sample of each of the following three commercially HAp-coated available dental implants were examined: Integral® (Calcitek, Inc., Carlsbad CA) 10 mm length, 4 mm diameter; Steri-OSS® (Denar Comp., Anaheim CA), 7 mm length, 4 mm diameter; IMZ-Lamellar® (Interpore, Inc., Irvine CA) 11 mm length, 4 mm diameter.

All implants were kept in their sterile packages upon evaluation. Samples of synthetic TCP (Synthograft®, Johnson & Johnson, NY), polycrystalline synthetic HAp (Calcitite®, Calcitek, Inc., Carlsbad CA) and synthetic amorphous calcium phosphate (provided by Interpore Int.) were used as reference materials. The samples were examined on normal microscopic slides. Special precautions against damage to the small crystals due to the heating by the laser light are normally not required when examining ceramics. At the power levels used in this study (< 25 mW at the sample) no damage was noted.

The instrument conditions used in recording these spectra were: spectral slit width, 2.7 cm^{-1}; laser power at sample, *ca.* 20 mW; exciting wavelength 514.5 nm. Microspectra and macrospectra were recorded with laser spot diameters of about 5 and 100 μm respectively.

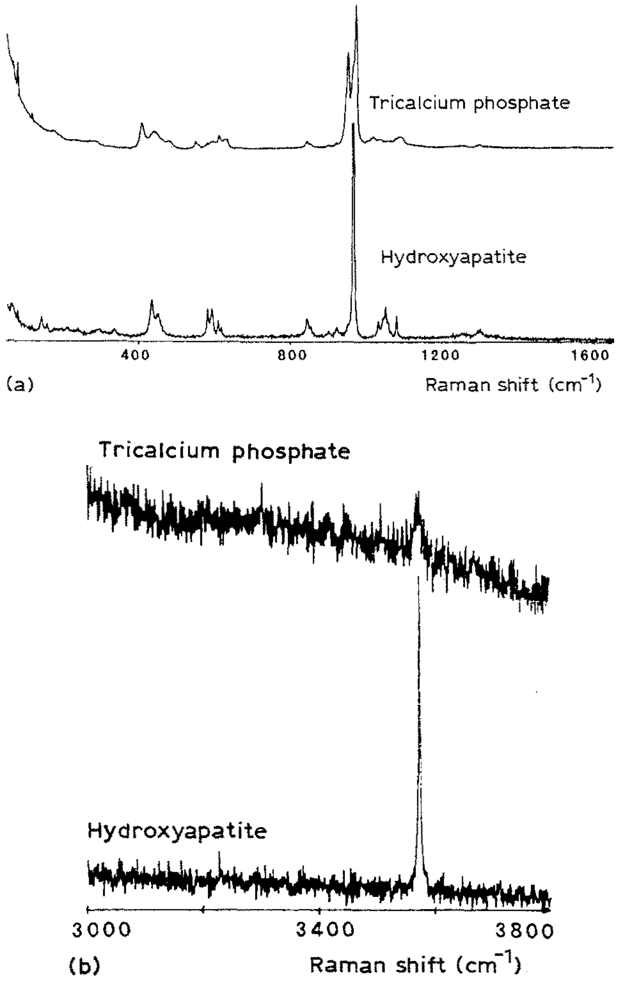

Figure 1 (a) Raman microprobe reference spectra of tricalcium phosphate and hydroxyapatite between 50 and 1650 cm^{-1}. Spectra were acquired with laser radiation at 514.532 nm, *ca.* 5 mW at sample, 300 μm slits, 100 x objective, scanning.1 $\mathrm{cm}^{-1}\,\mathrm{s}^{-1}$ per data point. (b) Raman microprobe reference spectra acquired between 3000 and 3800 cm^{-1}. Same conditions as in (a).

3. Results

Raman spectra of calcium phosphates represent inelastic light scattering from vibrations of atoms bound together by molecular forces of solidification [13]. For most analytical purposes the spectrum on the long wavelength or low energy side of the laser is examined (Stokes scattering). The difference in energy (plotted in cm^{-1}) corresponds to the vibrational energy of the molecules in the unit cells. Complete spectra of the two reference materials (HAp and TCP) are shown in Fig. 1. Fig. 1a shows spectra in the fingerprint region, and Fig. 1b shows spectra in the OH stretching region. The spectrum of HAp reproduces that previously reported where the spectrum was interpreted in terms of the C_{6h}^{2} space group instead of the C_{6}^{6} space group [22]. Apparently the lowering of symmetry produced by the position of the OH-groups in the unit cell does not affect the coupling of the phosphate vibrations. The symmetric phosphate stretch, $\surd 1$, appears as a single line at 964 cm^{-1}. Other bands were split by effects of packing of the ions in the crystal. The bands between 425 and 450 cm^{-1} have been assigned to components of $\surd 2$, those between 575 and 615 cm^{-1} were assigned to $\surd 4$ and those between 1025 and 1085 cm^{-1} to $\surd 3$ [22]. Initially it was thought that variations in the performance of the implants might be due to deposition of small amounts of TCP in place of some of the HAp. Therefore the reference spectra were recorded to determine the best region of the spectrum to be used for determination of TCP. The low intensity in the OH stretching region of TCP is consistent with the absence of OH groups in its composition; the residual intensity at 3574 cm^{-1} verifies previously reported HAp impurities in the TCP reference material [23]. It was apparent that the PO_4^{-2} symmetric stretching region near 950 cm^{-1} presents the most sensitive region for diagnostics of phase. Raman microprobe spectra of the implants subsequently were recorded in this region.

The spectra of the implants are overlaid with that of the reference materials in Figs 2 and 3. All the implants gave more or less the same characteristic spectrum. The strong phosphate band of HAp dominates the spectrum of the implant. All bands are broader than bands of the reference materials. However, there always appeared another band at lower frequency in the spectra of the implants (Fig. 2, arrow at 952 cm^{-1}). This extra band at 952 cm^{-1} does in fact overlap with a band of TCP, but is not assigned to TCP for the following reason. The TCP spectrum shows another band, of even greater intensity, on the high frequency side of the HAp band which was absent in all implant spectra. Since there is always the possibility that relative intensities of Raman bands can be distorted when single crystals are probed, several spectra of particles of TCP were examined and showed the same pattern as that in the figures. Therefore the extra low frequency band would have to be accompanied by a higher frequency band if its origin were TCP.

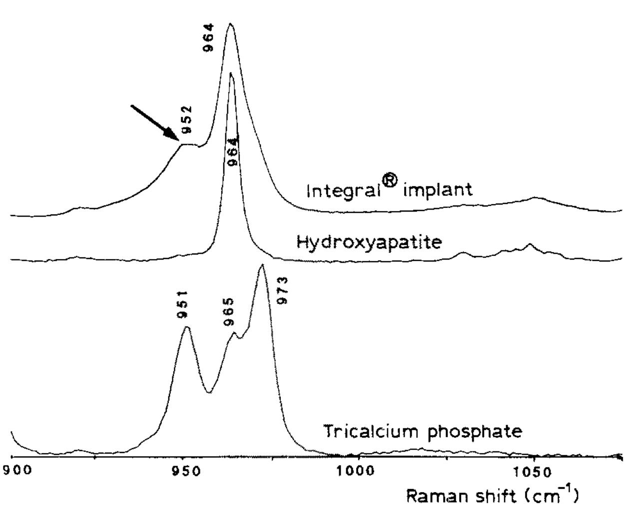

Figure 2 Raman microprobe spectra between 900 and 1075 cm^{-1} of reference materials and Integral® implant (arrow at low frequency band at 952 cm^{-1}).

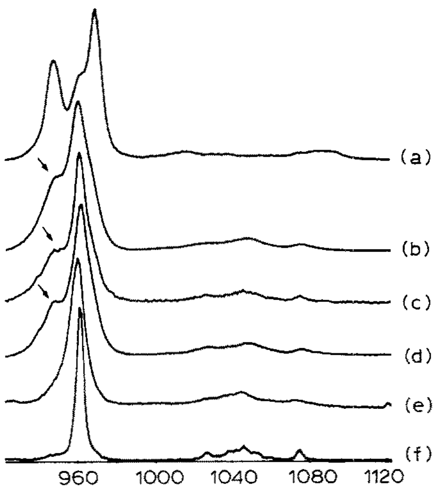

Figure 3 Raman microprobe spectra between 900 and 1120 cm^{-1} of reference materials including amorphous calcium phosphate and implants (arrows at low frequency bands at 952 cm^{-1}). (a) Tricalcium phosphate; (b) IMZ-Lamellar®; (c) Steri-OSS®; (d) Integral®; (e) amorphous calcium phosphate; (f) hydroxyapatite.

An alternative explanation for the extra band is that it comes from amorphous or microcrystalline material deposited during plasma flame spraying. It is known that the Raman spectra of the amorphous phases are analogous to spectra of the crystalline phase of the same material. The principle differences are that the bands of the amorphous phases are broadened; sometimes there is an enhancement of the low frequency side of the bands [24]. These effects arise from the reduction in size of ordered regions of the crystals and a breakdown of the selection rules due to the lack of translational symmetry. The resulting mesh in the Brillouin zone leads to scattering wave factors significantly different from zero, producing a spectrum of bands weighted by the phonon density of states [25]. This explanation, in fact, is consistent with the plasma spraying process, which is known to melt the particles. The reference spectrum of the powdered synthetic amorphous HAp reference material, however, did not exhibit the same low frequency sideband seen in the implant spectra (Fig. 3, arrows at 952 cm^{-1}). Another explanation for the extra low frequency band could be a structure within the sprayed amorphous phase. Such structural effects would result either directly from quenching from the plasma or by incorporation of titanium into the lattice during the plasma flame spraying process [27].

4. Discussion

It has been demonstrated in several experimental studies that the coating of titanium implants with hydroxyapatite or tricalciumphosphate resulted in bone formation around these implants which was superior in terms of amount and maturity, compared with titanium implants of a similar macroscopic design [14, 26, 30]. CPC-coated titanium implants demonstrated bonding strength at the implant bone interface which was five to six times stronger than with comparable titanium surfaces [14, 30]. Although one study revealed a decreasing bonding strength between the 12th and the 32nd week, the resulting strength still was three times higher than with a comparable titanium surface [14].

The results of our study indicate a considerable amount of amorphous or glassy material in these coatings. In one study crystalline hydroxyapatite was only observed occasionally in the outer ceramic layer of the coating [31]. The coating itself showed histological signs of biodegradation and resorption [31]. Other reports indicate a coating of high crystallinity (80%) but also report decreased interfacial shear strength after *in vitro* ageing of the coating in agitated Ringer solution [19]. Differences in the amount of glass phases are dependent on the technique and conditions of plasma flame spraying and obviously differ from product to product. During the plasma flame spray coating process, obviously, a considerable amount of the coating is deposited in an amorphous glass phase. This glass phase is reported to be a major consideration in the still controversial field of CPC bioresorption. Studies of biodegradability of CPC remain controversial. Materials with Ca/P ratio between 1.50 (i.e. amorphous calciumphosphate, ACP) and 1.67 (HAp) have been extensively investigated [3, 7, 10, 13]. Factors presumed to correlate with the biodegradation of CPC that are mentioned most in the literature include density, molar Ca/P ratio, crystallographic structure, presence of amorphous phases and the degree of porosity. In particular, micropores (< 5 μm) and the presence of glassy material enhance the bioresorption rate [2, 10]. This phenomenon of bioresorption is probably related to the crystals becoming disconnected through a solution-mediated resorption of glassy material. These glassy materials are presumably located at the grain boundaries. This initial breakdown is followed by phagocytosis of crystalline fragments [2].

Evidence of this hypothesis has been the observation of multinuclear cells of the foreign body type with incorporated ceramic fragments in close proximity to dense hydroxyapatite implants [9].

The second impact of amorphous glassy material on hydroxyapatite coatings is the increasing titanium–hydroxyapatite bonding strength with the increasing amount of amorphous glass phases [32].

ACP, which autocatalytically converts in water to a finely divided, non-stoichiometric hydroxyapatite tends with time in solution to improve slowly in stoichiometry and crystal size. The lack of stoichiometric and crystallographic uniformity contributes to a solubility which is higher than the solubility product of well-crystallized, stoichiometric HAp. In the transformation of the amorphous to microcrystalline HAp, the former phase may solubilize and renucleate as the crystalline phase [29]. In the formation of bone, first the organic matrix is deposited extracellularly and then it becomes infused with bone apatite. ACP is a precursor seen in the formation of bone apatite which transforms to poorly crystallized HAp. The most distinguishing feature of bone apatite is its small crystallite size and its lack of crystal and chemical uniformity. This makes for a reactive material which satisfies the teleological need for normal resorption and redeposition. Therefore ACP possibly plays a role in the solid solution equilibrium between bone and implant and facilitates the biological apatite deposition on the implant surface.

5. Conclusion

Raman microprobe spectra of HAp coatings on dental implants confirm that the deposition of hydroxyapatite during plasma flame spraying produces poorly crystalline HAp. Codeposited with crystalline HAp is a second phase, probably an amorphous glass phase of calcium phosphate. The relative amounts of crystalline HAp to amorphous calcium phosphate can be monitored by the Raman microprobe. The acquired spectra give no indication for tricalciumphosphate impurities in the plasma flame spray coating.

The role of amorphous calcium phosphates on endosseous dental implants deposited during the plasma flame spraying process requires further investigations in terms of bioresorption and impact on biointegration.

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