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SCANNING ELECTRON MICROSCOPY STUDIES OF CERAMIC LAYERS AND INTERFACIAL REGIONS FOR CALCIUM PHOSPHATE-COATED TITANIUM DENTAL IMPLANTS

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Abstract

The surface and cross-section characteristics of the plasma-sprayed calcium phosphate coatings, along with the microstructures and elemental compositions near the titanium alloy interface, were investigated by scanning electron microscopy for two different dental implants of proprietary compositions: Integral® (Calcitek) and Bio-Vent® (Dentsply). Elemental concentrations (Ca, P, Ti, Al, and V) near the interfaces were obtained by X-ray energy-dispersive spectroscopy. Coating surfaces exhibited a splat deposition topography of greatly differing microstructural scale for the two implants, along with other features characteristic of the plasma-spraying process; cross-sections of the coatings revealed minimal porosity. Some interdiffusion of principally titanium and calcium was found within a narrow region near the ceramic-metal interface, perhaps contributing to chemical bonding.

Key Words: Hydroxyapatite, calcium phosphate, plasma-spraying, titanium alloys, dental implants, biomaterials, ceramics, biocompatibility, scanning electron microscopy, X-ray energy-dispersive spectroscopy.

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Introduction

Osseointegration, i.e., the intimate adaptation of the implant material to bone, and clinical success have been achieved with endosseous dental implants, as a result of suitable materials selection, appropriate implant designs and atraumatic surgical procedures (Brånemark, 1983; Zarb and Schmitt, 1989, 1990a, 1990b, 1990c). Current endosseous implants are fabricated from commercially pure titanium or Ti-6Al-4V alloys, because of the outstanding biocompatibility of titanium (Kasemo and Lausmaa, 1985). For some commercial products, the titanium alloy is coated with a thin ($\sim 50 \mu\text{m}$) layer of hydroxyapatite (HA), which is deposited by a plasma-spraying process (de Groot *et al.*, 1987). Hydroxyapatite is the principal inorganic constituent in bone and tooth structure (Jarcho, 1986) and these coatings minimize release of metallic ions from the implant into the surrounding tissues (Ducheyne and Healy, 1988a), a matter of some controversy (Bruneel and Helsen, 1988). However, the possibility that the ceramic coatings may excessively harbor oral microorganisms has also been speculated (Johnson, 1992).

In plasma-spraying, starting powder particles are melted by a high temperature plasma generated from a carrier gas by the plasma gun, and the molten particles are rapidly deposited onto a substrate (Smart and Catherall, 1972; Zaat, 1983; de Groot *et al.*, 1987). The impacts of the molten droplets on the substrate yield a characteristic morphology termed **splat deposition**, and the coating is formed by the overlapping and coalescence of these deposits (Herman, 1988). While details of the starting powder particle compositions and the plasma-spraying parameters are proprietary information, the implant coatings are known to have a complex multiphase structure due to the non-equilibrium nature of the deposition process. In addition to HA, the coatings contain α and β tricalcium phosphate (TCP), calcium pyrophosphate, and a non-crystalline (amorphous or glassy) or microcrystalline constituent (Ducheyne *et al.*, 1986, 1988; Ducheyne and Healy, 1988b; Koch *et al.*, 1990; Klein *et al.*, 1991). Thus, while the **HA/TCP-coated implants** terminology is often employed in dentistry,

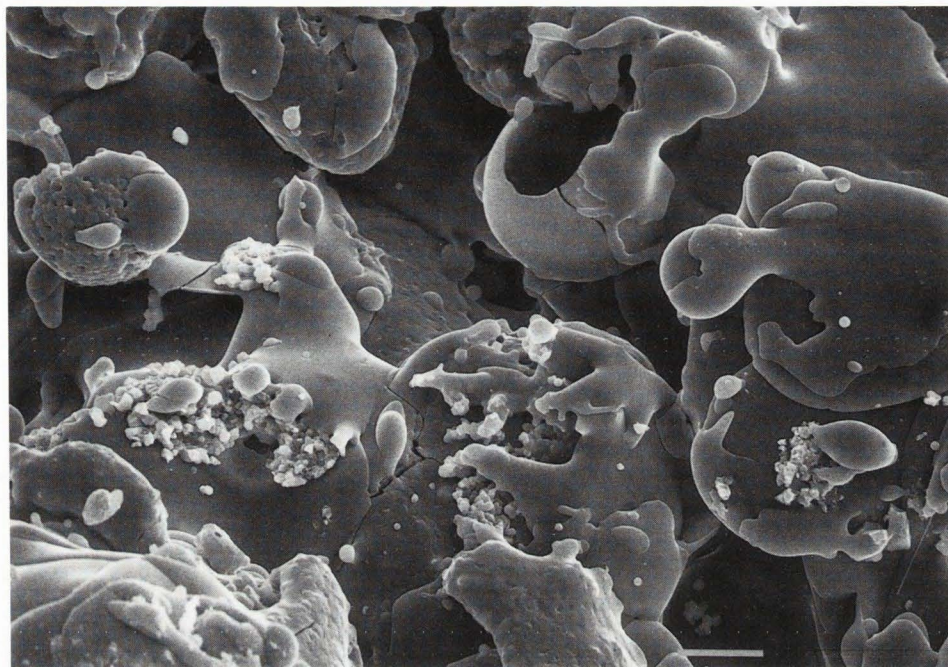


Figure 1. Secondary electron image of the surface of the plasma-sprayed coating for a BioVent® (Dentsply) implant. Bar = 10 μm .

The implant surfaces in Figures 1, 2, and 3 were coated with a thin Au-Pd film.

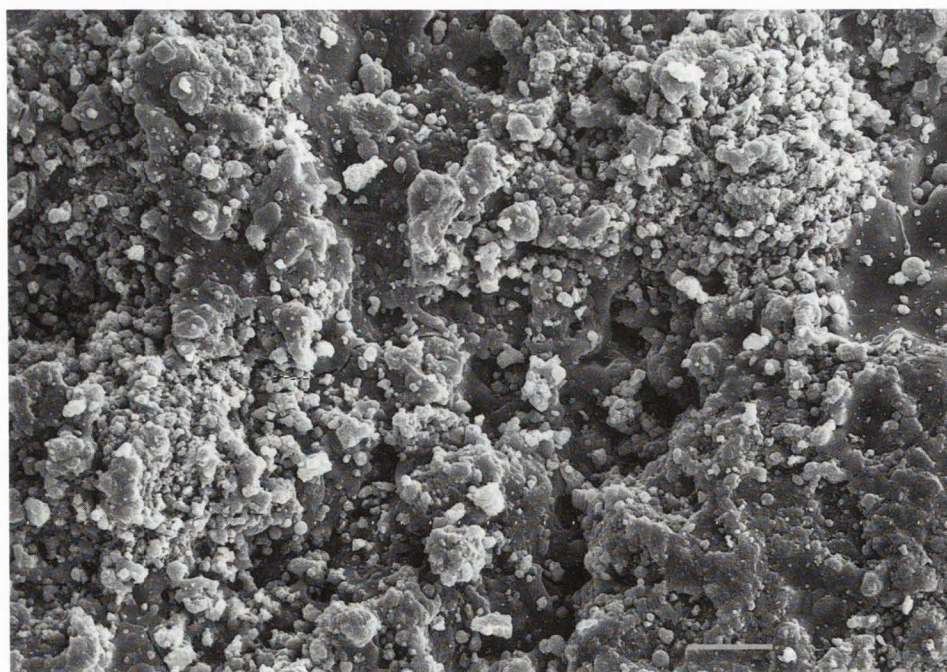


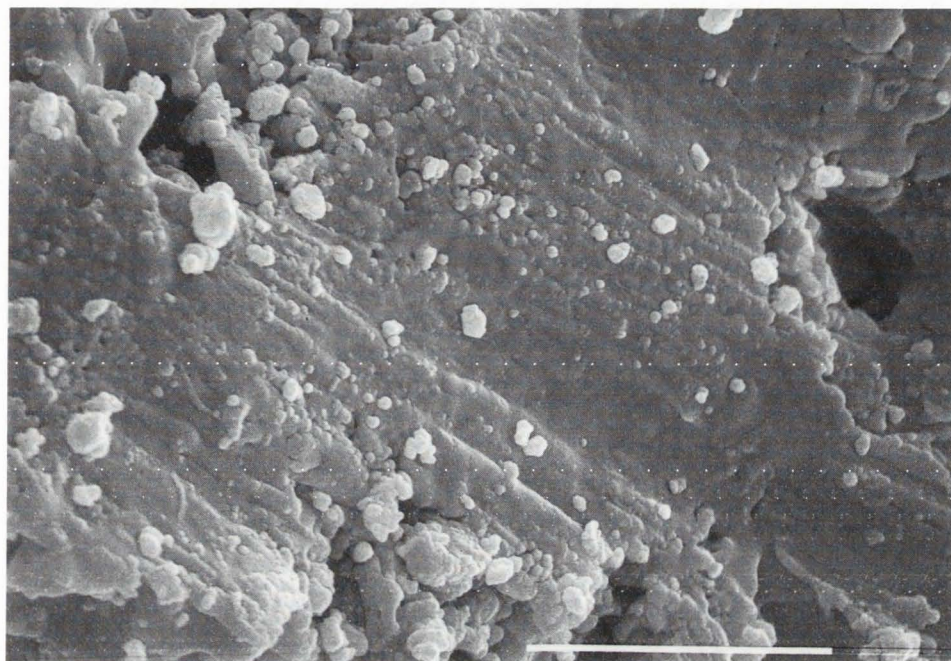
Figure 2. Secondary electron image of the surface of the plasma-sprayed calcium phosphate coating for an Integral® (Calcitek) implant. Bar = 10 μm .

the general nomenclature of calcium phosphate-coated implants is more appropriate.

Although, the chemistry of calcium phosphate bioceramics under equilibrium conditions has been studied extensively (de Groot *et al.*, 1990a; LeGeros, 1991) and several articles have been published on plasma-sprayed calcium phosphate-coated titanium alloys (Cook *et al.*, 1988; Berndt *et al.*, 1990; de Groot *et al.*, 1990b; Wolke *et al.*, 1992; Chen *et al.*, 1994), little microstruc-

tural information is available about commercial plasma-sprayed calcium phosphate-coated implants. The objective of the present research was to employ scanning electron microscopy (SEM) to characterize the coating surfaces, cross-sections, and interfacial regions with the titanium alloy substrates for two representative products. X-ray energy-dispersive spectroscopy (EDS) was used to estimate the extent of interdiffusion for the principal component elements in the coatings and substrates.

Figure 3. Secondary electron image of the surface of the plasma-sprayed coating for an Integral® implant. The striations in the center may be due to a phase transformation. Bar = 10 μm .



Materials and Methods

Integral® implant cylinders (Calcitek, Carlsbad, CA), 4 mm diameter x 15 mm height, and Bio-Vent® implant cylinders (Dentsply Implant Div., Encino, CA), 3.5 mm diameter x 16 mm height, were selected for study. While precise composition information is proprietary, both commercial products have plasma-sprayed calcium phosphate coatings on Ti-6Al-4V substrates. For SEM observations (JEOL JSM-820, JEOL Ltd., Tokyo, Japan) of the surfaces, two randomly selected cylinders from each manufacturer were removed from the sealed container provided for the as-received implants and sputter-coated with a Au-Pd film.

Representative surface regions for the body and tip of each implant were observed and photographed at a standardized magnification of 1,000x, and quantitative microscopic analyses using point counting and ruled grids (Vander Voort, 1984) were performed to obtain the percentage of incomplete surface coverage for the Integral® and Bio-Vent® products. The number of particles lying at the intersection points on a square grid were divided by the total number of points on the grid to yield the lineal fraction (volume fraction) of a microstructural feature. Five randomly selected areas were examined on at least three different photomicrographs of the surface and cross-section for each brand of implant. The results from point counting were checked qualitatively by comparison to published charts for estimating volume fraction. Student's *t*-test was employed for statistical analyses of the quantitative microstructural data for the two implants.

For characterization of the bulk coatings and interfa-

cial regions, three additional randomly selected cylinders from each manufacturer were embedded in transparent LR White acrylic resin (London Resin, Hampshire, England), using vacuum-impregnation and thermal curing at 50°-60°C. Each cylinder was sectioned parallel to the axis, utilizing a slow-speed (~ 100 rpm) saw (Isomet, Buehler, Lake Bluff, IL), a diamond-coated (low concentration) wafering blade and an oil-based blade lubricant (Isocut, Buehler). The sectioned specimens were ultrasonically cleaned in ethanol, wet-ground at ~ 100 rpm with 1000 grit and 4000 grit SiC papers, polished on cloth with OPS® or OPU® colloidal silica (Struers, Westlake, OH), and again ultrasonically cleaned in alcohol prior to carbon-coating for SEM/EDS evaluation.

Concentrations of Ca, P, Ti, Al and V (wt. %) near the coating-substrate interface were obtained with a Link eXL microanalysis system having a PentaFET detector and 7.6 μm beryllium window (Oxford Analytical Instruments, High Wycombe, U.K.). Raster scans were performed at 5000x, using 9 kV accelerating voltage and 200 seconds live collection time (~ 30% dead time). For each region analyzed, the total X-ray photon counts exceeded 100,000, thereby yielding accurate elemental analyses (Lee, 1993). For each of the three sectioned specimens, analyses were obtained for two or three sites in both the coating and substrate at varying distances from the interface, in order to provide quantitative information about the elemental interdiffusion. Appropriate calculations (Tufekci, 1993) provided assurance that the elemental concentrations were not obtained from overlapping regions with the use of 9 kV accelerating voltage, and all raw data for elemental concentrations were subjected to the ZAF correction (Goldstein *et al.*, 1981).

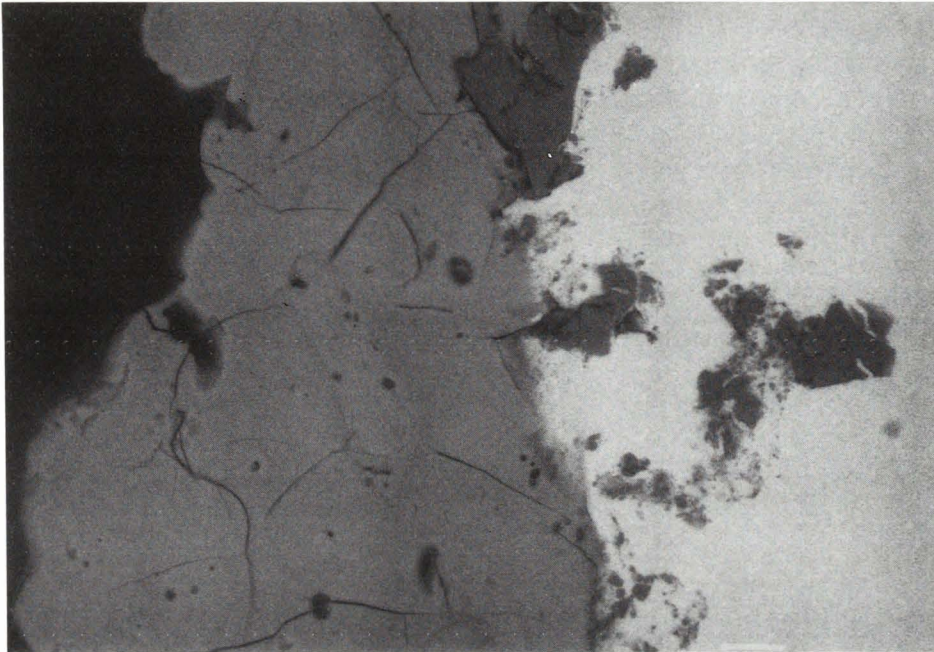


Figure 4. Backscattered electron image of the cross-section of a Bio-Vent® implant, showing the presence of alumina particles (dark regions) both adjacent to the interface and deeper within the substrate (right). The dark lines in the coating (center) may correspond to adjacent splat depositions, and the metallographic resin appears as a dark vertical region (left). Bar = 10 μm .

The specimens in Figures 4-7 were carbon-coated for EDS analyses.

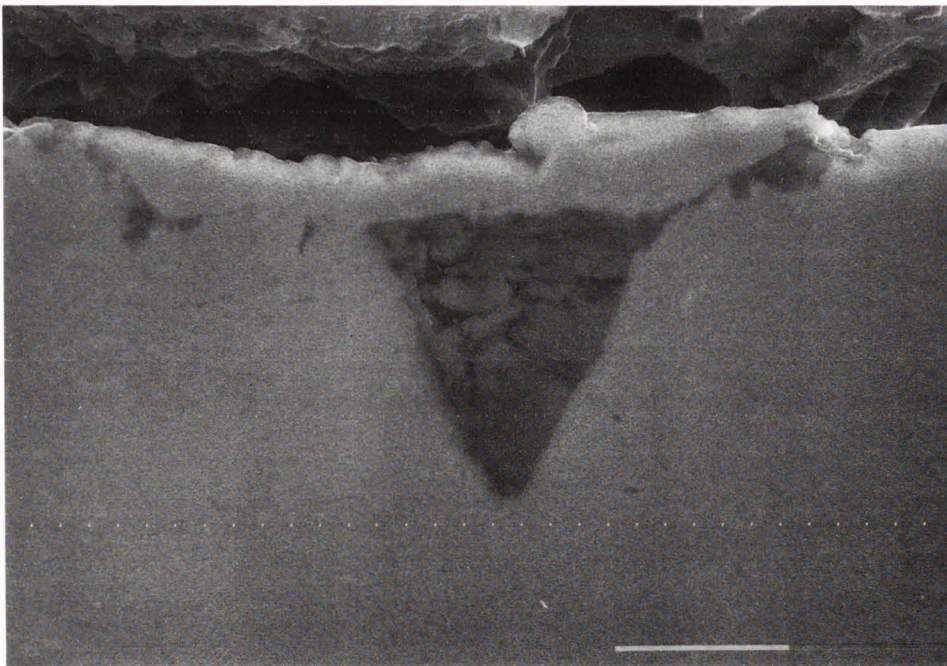


Figure 5. Secondary electron image of the cross-section of a Bio-Vent® implant, revealing a cluster of alumina particles (center) in the substrate near the interface. The gap between the coating (top) and the substrate may have been caused by the metallographic procedures. Bar = 10 μm .

Results

Representative photomicrographs of the coating surfaces are shown in Figure 1 for a Bio-Vent® (Dentsply) implant and in Figures 2 and 3 for Integral® (Calcitek) implants. The characteristic splat deposition surface morphology is evident, and regions can be seen where the deposited layers had incompletely coalesced. Comparison of Figures 1 and 2 show that the calcium phos-

phate coatings for the Integral® implants had a significantly ($P < 0.01$) finer surface microstructural scale than the coatings for the Bio-Vent® implants. Some surface cracks in the coatings are typically observed, and there are numerous unmelted or partially melted starting powder particles lying on the surfaces. A unique observation was a series of parallel surface striations on one Integral® implant specimen (Fig. 3).

Figure 6. Secondary electron image of the cross-section of an Integral® implant, showing the coating (center) and the interfacial region with the titanium alloy substrate (top). Polymerization shrinkage in the metallographic resin in the metallographic resin (bottom) has caused a gap adjacent to the coating. The dark-appearing regions (top center) are groups of alumina particles. Bar = 10 μm .

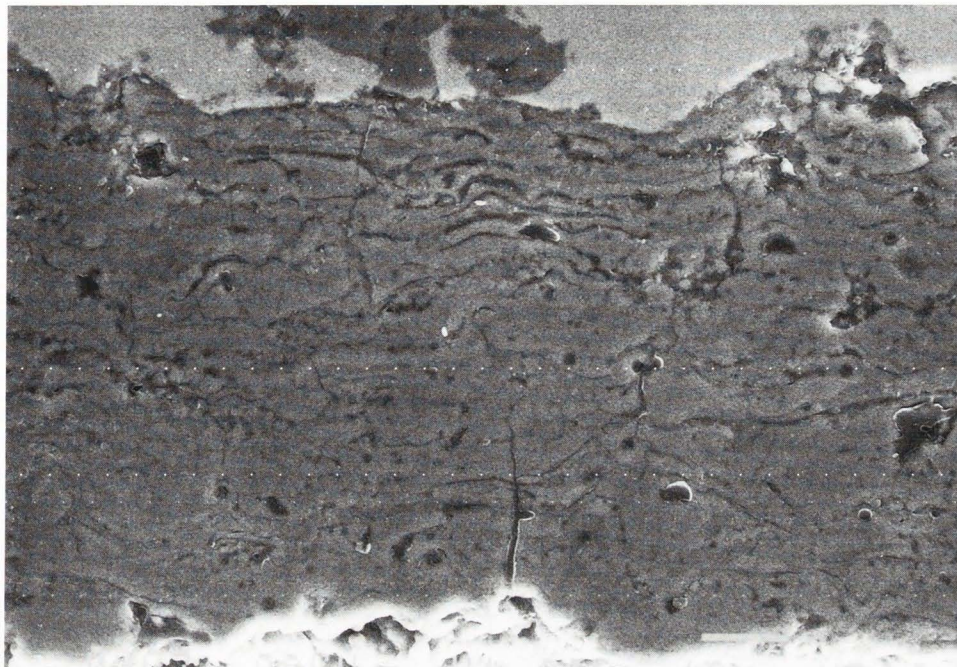
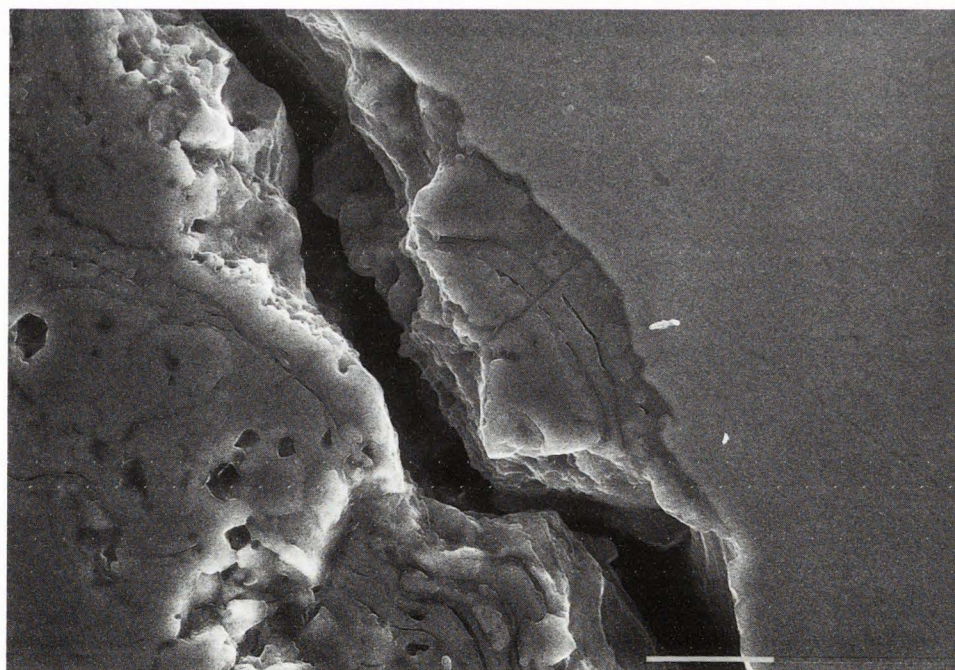


Figure 7. Secondary electron image of the cross-section of an Integral® implant, showing a fracture through the calcium phosphate coating. Bar = 10 μm .



The quantitative microscopic evaluations of these photomicrographs showed that the surfaces of the coatings might be considered to exhibit porosity exceeding 10%, if porosity is defined in terms of the areas where adjacent splat deposition regions failed to coalesce completely. However, representative photomicrographs of the cross-sections of the coatings and interfacial areas with the Ti-6Al-4V substrates in Figures 4, 5, and 6 showed that the bulk coatings for both implants con-

tained minimal porosity and that the coatings were intimately adapted to the substrates. Although a very small interfacial gap was typically observed for some Bio-Vent® implant specimens (Fig. 5), this gap was probably the result of metallographic specimen preparation, despite the considerable care taken with these procedures (Larson FG, private communication). In Figure 6, some lines in the Integral® implant coating appear to correspond to successively sprayed layers and other lines

appear to be boundaries between splat deposition regions. In addition, unmelted or partially melted starting powder particles can be observed at several sites within the bulk coatings in Figures 4, 5, and 6. A unique observation of a fracture through the calcium phosphate coating of an Integral® implant is shown in Figure 7.

For all sectioned specimens of both implants, irregularly shaped dark regions were observed in the metal substrates near the interface with the coating. Higher magnification observations revealed that these regions were invariably associated with an agglomeration of particles, as shown strikingly in Figure 5. Because EDS analyses indicated that these deposits were rich in aluminum and oxygen, it was assumed that the particles were residual alumina abrasives which are typically used by manufacturers in the preparation of the substrate surfaces prior to plasma deposition of the coatings (Larson FG, private communication).

The EDS analyses further established that limited elemental interdiffusion occurred within a narrow region on either side of the coating-substrate interfaces during the plasma-spraying process. Because the lengths of the parallel scans across the specimens were varied and the concentrations of the diffusing species were small, it was necessary to present the results in Tables 1 and 2 with conservative estimates of upper limits of the diffusion process. The data thus did not permit the calculation of interdiffusion coefficients. The titanium and aluminum concentrations in the coatings at a distance of 1.0-1.5 μm from the interface were less than 2 wt.%, while the vanadium concentration was below the limit of detection. In the substrates, the calcium concentration at a distance of 1-2 μm was less than 1 wt.%, while the phosphorus concentration was below the limit of detection.

Discussion

The coatings for both the Integral® and Bio-Vent® implants displayed the characteristic splat deposition morphology and microstructural features associated with plasma-spraying (Smart and Catherall, 1972; Herman, 1988). While significant differences in the microstructural scales for the two implants (Figs. 1 and 2) are indicative of different plasma-spraying processes, specific details remain proprietary with each manufacturer. Numerous variables must be controlled to achieve optimum coatings: the design and operating conditions for the plasma gun; the composition and flow rate of the carrier gas; the composition and size distribution of the starting powder particles; the method for introduction of the powder particles into the plasma; the distance between the plasma gun and the substrate; and the temperature of the substrate during deposition of the coating. Although

the molten calcium phosphate particles cool substantially prior to impinging on the substrate surface, these ceramic particles are reported to maintain temperatures in excess of 1300°C at deposition; this elevated temperature may promote the formation of an interfacial layer (Berndt *et al.*, 1990).

The relatively large number of unmelted or partially melted starting powder particles on the surfaces of both coatings suggest that the plasma-spraying conditions were controlled to minimize superheating of the molten calcium phosphate droplets impacting on the titanium alloy substrate. From the principles of ceramic science (Kingery *et al.*, 1976), this should increase the percentage of the crystalline calcium phosphate phases relative to that of the amorphous (glassy) phase, which is of considerable clinical importance. The relative proportions of these phases determine the *in vivo* interfacial bioactivity and resorption, as well as the physical and mechanical properties of the coatings and their *in vivo* stability.

Despite the presence of incompletely coalesced splat deposition regions, which are natural consequences of plasma-spraying, examination of the sectioned specimens indicated that the coatings contained relatively little bulk porosity (Figs. 4 and 6). The surface cracks found in the coatings (Figs. 1 and 2) might be anticipated, since the rapid cooling rates characteristic of plasma deposition create high internal stresses (Smart and Catherall, 1972). In industrial practice, the substrate is usually heated during plasma-spraying; although not common in the implant industry (Larson FG, private communication), post-deposition heat treatments might be performed to reduce residual stresses in the calcium phosphate coatings. The formation of cracks in the implant coatings should also depend upon the difference in the thermal contraction coefficients (when the titanium alloy substrate and the brittle ceramic cool to room temperature after completion of the plasma-spraying). A higher thermal contraction coefficient for the coating than the substrate (Moroi *et al.*, 1993) would subsequently create residual tensile stresses parallel to the interface and lead to cracks in the ceramic.

The bulk coatings appeared to be relatively free of cracks, although some apparent delamination fractures parallel to the interface were observed (Fig. 6). Even if these fractures were caused by specimen preparation procedures, this observation suggests that the boundaries between successive plasma-sprayed layers may be regions of relative weakness in the coatings. Numerous observations of the sectioned specimens established that the coating thickness varied from ~ 30 -100 μm for the Bio-Vent® implants and from ~ 50 -100 μm for the Integral® implants. The average coating thickness for both implants was in the approximate range of the 50 μm value previously reported by de Groot *et al.* (1987).

SEM studies of ceramic-coated dental implants

Table 1. Elemental concentrations at varying distances from the interface in sectioned specimens of the Bio-Vent® implant.

Element	Bulk substrate	5.0-3.3 μm from interface (substrate)	3.2-1.8 μm from interface (substrate)	1.7-1.0 μm from interface (substrate)	1.0-1.5 μm from interface (coating)	1.6-3.0 μm from interface (coating)	3.1-4.0 μm from interface (coating)
Ti	87.7 (3.0)	86.9 (0.1)	85.9 (2.8)	86.4 (1.2)	3.5 (0.8)	1.3 (0.1)	B.D.L.*
Al	8.6 (0.3)	9.7 (0.1)	8.5 (0.2)	9.5 (0.2)	1.7 (0.2)	B.D.L.	B.D.L.
V	3.7 (0.7)	2.8 (0.1)	5.0 (0.7)	3.4 (1.3)	B.D.L.	B.D.L.	B.D.L.
Ca	B.D.L.	B.D.L.	B.D.L.	0.6 (0.1)	72.6 (2.5)	69.6 (1.7)	69.5 (0.4)
P	B.D.L.	B.D.L.	B.D.L.	B.D.L.	22.0 (0.5)	28.9 (1.8)	29.6 (0.5)

*Analysis concentration is below instrumental detection limit.

Table 2. Elemental concentrations at varying distances from the interface in sectioned specimens of the Integral® implant.

Element	Bulk substrate	5.6-4.6 μm from interface (substrate)	4.5-2.6 μm from interface (substrate)	2.5-1.0 μm from interface (substrate)	1.0-1.5 μm from interface (coating)	1.6-3.0 μm from interface (coating)
Ti	88.2 (3.0)	83.6 (3.8)	85.8 (1.0)	86.4 (1.5)	1.8 (2.0)	1.0 (0.4)
Al	8.8 (0.3)	7.4 (1.5)	9.6 (0.5)	9.2 (0.3)	0.6 (0.4)	B.D.L.*
V	3.0 (0.7)	8.2 (5.1)	3.8 (0.7)	3.4 (1.2)	B.D.L.	B.D.L.
Ca	B.D.L.	0.5 (0.2)	0.6 (0.2)	0.9 (0.1)	71.1 (2.0)	72.2 (0.6)
P	B.D.L.	B.D.L.	B.D.L.	B.D.L.	26.6 (0.6)	26.4 (0.7)

*Analysis concentration is below instrumental detection limit.

This thickness is presumed to be a compromise between the more rapid *in vivo* loss of thinner coatings due to resorption and the lower adhesive/cohesive strength of thicker coatings (Kester *et al.*, 1991).

Because of their small sizes and similar Ca/P ratios, the calcium phosphate phases in the powder particles on the surfaces and in the bulk coatings could not be identified by EDS. Previously published morphological appearances of the crystalline phases (LeGeros, 1991) suggest that the parallel striations in Figure 3 may be due to a phase transformation during cooling of the plasma-sprayed coating from elevated temperatures (Koch *et al.*, 1990; Klein *et al.*, 1991). X-ray diffraction or transmission electron microscopy would be necessary to identify the crystalline phases and provide insight into any phase transformation processes.

The diffusion of titanium into the plasma-sprayed coatings was considerably less than that reported by Ducheyne *et al.* (1986) for HA coatings deposited on titanium by electrophoresis and sintered for 1 hour at 900°C. Nevertheless, the limited diffusion of the major component elements in the substrate and in the coating across the interface may provide a chemical component to the bond strength. In private communications, dental implant manufacturers have stated that the bond strength for the coating principally originates from mechanical retention, and the level of roughening for the substrate surface can be seen in Figures 4, 5, and 6.

An important closing observation is that their minimal bulk porosity and intimate adaptation to the substrates for both implants suggest that these coatings should not excessively harbor oral microorganisms or

provide facile pathways for the migration of such microorganisms to the surrounding tissues under *in vivo* conditions. However, Johnson (1992) has presented anecdotal case report data indicating concerns with the clinical use of calcium-phosphate coated implants. The relationships between oral microorganisms and clinical implant failure are complex (Mombelli *et al.*, 1987; Becker *et al.*, 1990; Haanaes, 1990), and further fundamental research in this area is needed. Several long-term studies are currently underway in our College of Dentistry to evaluate the clinical efficacy of coated dental implants (McGlumphy *et al.*, 1993).

Conclusions

Scanning electron microscopic examination of two commercial endosseous dental implants showed that the plasma-sprayed calcium phosphate coatings had a characteristic splat deposition morphology. While significant differences in the scale of these microstructural features were indicative of variations in the proprietary plasma-spraying conditions for the two implants, the presence of numerous unmelted or partially-melted particles on the coating surfaces suggested that these conditions were controlled to minimize superheating of the molten powder particles. Surface cracks which occur when the molten particles resolidify to form the coatings may be attributed to several factors: high residual stresses and rapid freezing rates from the plasma deposition process, differences in the thermal contraction coefficients of the coatings and the Ti-6Al-4V substrates, and the brittle character of the calcium phosphate constituents in the coatings. Examination of sectioned implants revealed that the coatings were approximately 50 μm in thickness, contained little bulk porosity, and exhibited relatively intimate adaptation to the substrates. Limited diffusion of titanium, aluminum and calcium was found within a narrow region around the coating-substrate interface and may contribute a chemical component to the coating bond strength. Although the present *in vitro* results suggest that the coatings would not excessively harbor oral microorganisms or provide pathways for the movement of these microorganisms to surrounding tissues *in vivo*, further research in this area is needed.

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Discussion with Reviewers

J.C. Keller: How are the authors certain that the EDS analyses at the interfaces of the sectioned specimens do not contain significant errors in the elemental concentrations because of cutting and smearing effects of the surfaces during specimen preparation?

Authors: Great care was taken with the cutting and polishing of the specimen surfaces to avoid this problem, and there was substantial consistency among all of the EDS data. The limited elemental interdiffusion at the coating-substrate interfaces in the present studies was consistent with the greater interdiffusion found by Ducheyne *et al.* (1986) for HA coatings deposited on titanium by electrophoresis and sintered for 1 hour at 900°C.

J.C. Keller: Why did the authors not perform X-ray diffraction to identify the crystalline phases and determine the percentage of the amorphous phase in the coatings?

Authors: We agree that it is essential to perform X-ray diffraction analyses of the coatings, and extensive research is underway in this area for a separate publication.

J.C. Keller: Would the location of the Al-rich areas

(alumina particles) below the surface of the titanium alloy substrates be an expected occurrence from sand-blasting?

Authors: The surprising discovery of alumina particles substantially below the interface with the titanium alloy substrate suggests that the manufacturers use a relatively high air pressure for grit-blasting the substrate surface prior to plasma-spraying the calcium phosphate coating.

Reviewer V: Could errors be introduced in the series of EDS spot analyses for elemental concentrations near the interface by the occurrence of overlapping interaction volumes?

Authors: We were aware that overlapping interaction volumes will create spurious results with a series of closely spaced SEM/EDS spot analyses if too high an accelerating voltage is used. Our calculations indicated that no problem of this type existed with use of the 9 kV accelerating voltage.

Reviewer V: Do the authors feel that the oral microorganisms will penetrate the surface cracks and remain in the coatings under clinical conditions? Will this influence the stability of these coated implants in the oral environment?

Authors: The possibility of oral microorganisms existing in these coated implants is of great importance, and warrants further research to determine if the clinical longevity and efficacy of the implants are compromised as a result. Our scanning electron micrographs show that the surface cracks do not extend greatly into the bulk coatings. We are unable to state whether specific cracks observed in sectioned specimens are due to manufacturing processes or our metallographic preparation techniques.