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Materials Engineering Approaches Towards Advanced Bioceramic Coatings on Ti6A14V Implants

Robert B. HEIMANN[1], Khemchai HEMACHANDRA[2], and Pibul ITIRAVIVONG[3]
[1]Chair of Technical Mineralogy, Department of Mineralogy,
Freiberg University of Mining and Technology
[2]Department of Materials Science, Faculty of Sciences, Chulalongkorn University
[3]Department of Orthopedics, Faculty of Medicine, Chulalongkorn University

Abstract

In this contribution several approaches towards engineering of bioceramic coatings applied by thermal spraying to titanium alloy substrates are being described. Optimization of plasma spray parameters can be used to deposit coatings with controlled porosity, high adhesive strength and optimum crystallinity. Microstructural engineering of the hydroxyapatite powder by pre-spray annealing leads to a substantial decrease of the microporosity of the ceramic grains. Moreover, bond coats based on titania and zirconia are being used to control the rate of heat transfer from the molten particles to the substrate and hence to improve the resorption resistance by suppressing the deposition of amorphous calcium phosphate (ACP).

Introduction

The number of patients receiving biomedical implants to correct skeletal defects is constantly increasing worldwide. Large demand exists for hip endoprosthetic implants, dental implants, and bone replacement parts in the maxillar-mandibular area, the ossicular chain of the inner ear, and alveolar ridge and iliac crest augmentation. For example, in Germany the annual number of total hip replacements has grown to about 85,000 and counting (Lugscheider and Knepper, 1993). In the United States, in 1986 alone the number of skeletal implants reached 300,000 with a total sales volume of over 1 billion dollars (Halter and Yamamoto, 1988).

State-of-the-art for hip implants is the use of Ti6A14V shafts plasma-spray coated with hydroxyapatite and equipped with an alumina or stabilized zirconia ball that articulates against an acetabular cup anchored in the hip bone, and made from titanium and lined with ultrahigh molecular weight high density (UHMWHD)-polyethylene to assure a low coefficient of friction (Figure 1). Increasingly, acetabular cups with inserts made from alumina are used that articulate against an alumina ball, for example in designs developed by CeramTec AG, Plochingen, Germany. The tribological pair alumina-alumina exhibits a particularly low coefficient of friction.

While this technology is well developed and clinically solidly established, less agreement has been reached among surgeons on the functional performance and, indeed necessity of the plasma-sprayed hydroxyapatite coating on the titanium alloy shaft anchored in the top part of the femur. The general idea is to provide an about 100-200 μm thick porous coating into which bone cells would grow and thus improve the anchoring to the surrounding living tissue. The bioactive hydroxyapatite elicits a specific biological response at the interface of the material by control of its surface chemistry resulting in the formation of a strong osseoconductive bond between tissue and biomaterial. According to the definition by Hench and Ethridge (1982), *bioactive materials* such as several calcium phosphates, bioglasses and glass ceramics not only interact with the body by stimulating osseointegration, *i.e.* incorporation of the implant into the living bone tissue, but will sometimes also be resorbed and transformed to calcified osseous tissue. Hence the dominant biorelevant mechanism is bonding osteogenesis that is characterized by a true chemical bond between implant and bone. On the other hand, *bioinert materials* such as alumina, zirconia and carbon as well as some metals such as titanium or tantalum react with the host tissue by contact osteogenesis that is characterized by a direct, simply mechanical contact between implant and bone. Finally, *biotolerant materials* such as PMMA bone cement, stainless steel, cobalt chromium alloys and even wood will be accepted by the body and develop an implant interface characterized by a layer of space filling connective tissue separating implant and bone, and thus providing distance osteogenesis.

With this background, intense research is ongoing worldwide to improve the mechanical and biological performance of materials utilized in biomedical applications. Such activities are centred on the development of materials with longer lifetime in the human body for existing bioengineering solutions such as hip endoprostheses, and also materials that in novel devices can serve completely new functions including remediating diseases of the skeleton and the joints such as osteoporosis and arthritis. Bioinert load-bearing ceramic parts such as the ball joints of hip endoprostheses fabricated from alumina or stabilized TZP zirconia, bioactive non-load bearing materials for filling bone cavities in the maxillar-mandibular area or for reconstructing the ossicular chain of the inner ear, as well as bioactive ceramic coatings with improved mechanical properties and interfacial chemical control play a particularly important role (Hench and Wilson, 1993). Ideally, biomaterials introduced into the body should possess self-repair capability but this is not possible yet with the materials classes in use. Problems also exist with mechanical and chemical performance since presently most patients will outlive the expected lifetime of their prostheses, a fact that necessitates costly, and physically and mentally stressful remediation operations (explantation). The probability of explantation is fortunately rather low, in the range of 1 to 10%, depending on the type of implant (Kock, 1995). Moreover, there is the general problem of the inherent instability of the interface between the implant and the host tissue. This instability can manifest itself in two ways.

(i) The formation of a non-adherent fibrous capsule in contact with bioinert or biotolerant materials causes local stress concentrations due to movement of the implant within the capsule. A gap can develop between implant and bone into which acellular connective tissue can invade. This may lead to aseptic loosening. Besides from being painful to the patient, the process may eventually cause the bone and/or the implant to fracture.

(ii) Since there is a mismatch in the Young's moduli of the bone and the implant material, most of the load produced by the body weight is being carried by the metallic implant, not the bone. The result is so-called 'stress shielding' of the bone. Since bone tissue must continuously be subject to tensile load to remain functional and healthy, this stress shielding can cause bone resorption.

The functionality of bioceramic materials introduced into the body requires stringent control at two levels of performance: mechanical and chemical. The use of ***bioinert ceramic materials*** instead of metals as balls for hip endoprostheses (i) prevents metallic corrosion products to enter the body that have been shown to induce impaired development of human osteoblasts (Tomas, *et al.* 1996), (ii) provides a high load-bearing potential and (iii) high wear resistance, as well as (iv) a low friction coefficient when articulating against the acetabular cup made from titanium and lined with ultrahigh molecular weight-high density polyethylene (UHMWHD-PE), or alumina. This is essential since the absence of the lubricating synovial fluid in the natural hip joint, requires excellent surface properties with regards to the tribological performance of the system. There is, however, no solution to the problem of the instability of the interface with regards to stress shielding since the rigidity of the ceramic materials considerably exceeds that of the bone.

The biomaterial-bone interface

Bioactive ceramic materials such as hydroxyapatite, bioglasses, and apatite-wollastonite (A/W) glass ceramics promote the formation of a tight bond between the ceramics and the bone tissue by bonding osteogenesis mediated by interfacial chemical control (Kasemo and Lausmaa, 1986). Chemical reactions occur in contact with body fluid that are comparable with the natural repair mechanism of the tissue. Hence, no fibrous capsule forms and bonding is achieved by bonding osteogenesis. According to the rate of bonding three processes can be distinguished (Gross, *et al.* 1988). Bioglasses of the quaternary system Na_2O-CaO-P_2O_5-SiO_2 with 45-52 mass% SiO_2 possess Class A bioactivity characterized by rapid bonding with a high rate of proliferation of bone cells (osteoproduction). Bioglasses with 55-60 mass% SiO_2 show much slower bonding (Class B bioactivity, osteoconduction). Finally, hydroxyapatite bulk ceramic or coatings develop only very slow bonding rates (osteointegration) (Jarcho, *et al.* 1977).

There is still much to be learned about the nature of the biomaterial-tissue interface. This lack of knowledge is a major barrier to the sucessful development of more advanced biomaterials and implants. The surface of the biomaterial is not just a passive boundary separating the tissue from the adjacent volume filled by the biomaterial. Instead, extremely complicated biochemical reactions occur in the very interface region that appears to be covered by a layer of extracellular matter including water molecules, electrolyte ions, and biomolecules of yet unknown composition. The situation is further complicated by the fact that the evolution with time of the interface has to be taken into account. Figure 2 shows a hypothetical scenario of the dynamic behaviour of the interface developed by Kasemo and Lausmaa (1991). This scenario emphasizes that the interfacial area is subject to development at all spatial and temporal levels, from the molecular to the cell to the tissue morphology levels, as well as from the first second up to several years after implantation. The inset of Figure 2 shows that initially the implant is separated from the native tissue by a fluid spaces that becomes increasingly filled with newly formed bone cells, mediated by adsorption of proteins at the implant surface. Consecutively, bone tissue damaged by the trauma of the operation repairs itself within a time period of several weeks. While in most cases normal bone tissue is being formed, in other case connective tissue forms a fibrous capsule (Figure 2, inset) (Kasemo and Lausmaa, 1991). The model relies on the interaction with tissue of the native oxide layer covering the titanium alloy implant. If, however, a bioactive coating or a bioglass is included, calcium and phosphate ions as well as silanol groups are being provided as bonding sites for cation-specific nectin attachment complexes on progenitor cells. These cells may activate the cell membrane receptors that are involved in the differentiation of the cells into true osteoblasts with matrix vesicles that are able to produce type I collagen (Hench and Ethridge, 1982). These interactions of the bioactive material with progenitor cells may be associated with the activation of the genetic code of the cells, a mechanism that reaches deep into the earliest stages of the evolution of cells with specialized function (Hench, 1989).

Bioactive coatings based on calcium phosphate ceramics

Today bioceramic coatings based on hydroxyapatite are being routinely applied to titanium alloy hip endoprosthetic implants by thermal spray technologies, most notably atmospheric plasma spraying. To obtain bioactive coatings with controlled porosity and sufficient resorption resistance, their chemical purity, phase composition, crystallinity, fracture toughness, and cohesive and adhesive strengths must be carefully optimized. Since hydroxyapatite melts incongruently, the high temperature present in a plasma jet inevitably leads to its thermal decomposition into other calcium phosphates, e.g. tricalcium phosphate (TCP), tetracalcium phosphate (TetrCP) or even non-biocompatible calcia (CaO). The *in vivo* stability of coatings is being strongly affected by those decomposition products (Klein, *et al.* 1994). To improve the adhesion of the coating, the degree of melting of the hydroxyapatite particles must also be improved by an increase of the plasma enthalpy (McPherson, *et al.* 1995) (see also Scheme 1). These high enthalpies lead on the other hand to increased thermal decomposition and thus to a decrease of the resorption resistance, *i.e.*, the *in vivo* longevity of the coatings. As a consequence, the plasma spray parameters and the microstructure of the deposited coatings need to be carefully optimized by controlling the heat transfer from the hot core of the plasma jet to the center of the powder particle.

The improvement of the coating performance required in terms of (i) the adhesion of the coating to the substrate and (ii) the biological stability of the coating in contact with corrosive body fluids can be achieved in several ways.

(i) *Control of the intrinsic plasma spray parameters* with the aim to minimize the thermal decomposition of the hydroxyapatite powder in the hot plasma jet leads to coatings whose resorption resistance can be increased. The formation of tricalcium phosphate (TCP), tetracalcium phosphate (TetrCP) and amorphous calcium phosphate (ACP) will be suppressed. Since these phases are more soluble in the aggressive body environment compared to hydroxyapatite (Willmann, 1996), the overall resorption resistance of the bioceramic coating increases (Heimann, *et al.* 1997). For example, figure 3 shows x-ray diffractograms of coatings sprayed with identical plasma energies (42 kW), chamber pressures (100 mbar argon) and powder feed rates but varying spray distances (3A,B: 240 mm; 3C: 360 mm) and substrate temperatures (3A: preheated to about 600°C; 3B, C: non-preheated). The coating of figure 3A displays a high amount of the thermal decomposition products TetrCP (4) and non-biocompatible CaO (1). In non-preheated coatings (Figure 3B) little CaO could be observed but TCP (3) instead. Increasing the spray distance (Figure 3C) results in almost pure hydroxyapatite with only a trace of TetrCP. On the other hand, decreasing the plasma energy to 29 kW as well as increasing the chamber pressure to 200 mbar, *i.e.* shortening the plasma jet leads to coatings essentially free of contamination by thermal decomposition products. As shown by Raman spectroscopy, the intensity of the Raman shift at 3575 cm^{-1} associated with OH groups decreased in all samples investigated. This is due to partial (oxyhydroxyapatite, $Ca_{10}(PO_4)_6(OH)_{2-2x}O_x\square_x$) or complete (oxyapatite, $Ca_{10}(PO_4)_6O$) removal of hydroxyl ions from the structure of hydroxyapatite (Trombe and Montel, 1971). However, complete rehydroxylation is expected in contact with body fluid. The thermal dehydroxylation of hydroxyapatite occurs in three steps:

(ii) *Microstructural engineering* of the as-received hydroxyapatite by short-term annealing at 1300°C leads to a substantial reduction of the microporosity. Since the porosity of the powder can be transferred to the coating this pre-spray annealing reduces the coating porosity with an associated increase in adhesive strength and resorption resistance (Heimann and Vu, 1997). Figure 4 shows SEM micrographs of an as-received hydroxyapatite grain (A) and a grain annealed at 1300 °C for 1 hour (B). The decrease in microporosity of the powder during sintering leads to much denser coatings.

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_{2-2x}O_x\square_x + x\,H_2O \qquad \text{....(1)}$$

$$Ca_{10}(PO_4)_6(OH)_{2-2x}\,O_x\square_x \rightarrow Ca_{10}(PO_4)_6O + (1-x)\,H_2O \qquad \text{....(2)}$$

$$Ca_{10}(PO_4)_6O \rightarrow 2\,Ca_3(PO_4)_2 + Ca_4(PO_4)_2O \qquad \text{....(3)}$$

Scheme 1 summary of the trends obtained by optimization of the plasma spray parameters.

- Suppression of thermal decomposition

$$\eta\downarrow, T_s\downarrow, P\uparrow, m\uparrow, x\uparrow \quad \therefore \quad E\downarrow$$

- Reduction of coating porosity

$$\eta\uparrow, T_s\uparrow, x\downarrow \quad \therefore \quad E\uparrow$$

- Increase of coating adhesion

$$\eta\downarrow, T_s\uparrow, x\downarrow \quad \therefore \quad \sigma\downarrow$$

The symbols are η = plasma current, T_s = substrate temperature, P = chamber pressure, m = powder feed rate, x = spray distance, E = plasma enthalpy, and σ = residual coating stress.

Scheme 1

(iii) Application of *biocompatible bond coats* whose interfacial interactions with the hydroxyapatite top coat and the Ti alloy substrate provide substantially increased adhesive strength as well as act as thermal barrier coatings to enhance the crystallinity of the deposited bioceramic coating system (Kurzweg, *et al.* 1998; Lamy, *et al.* 1996). Figure 5 shows a cross-sectional SEM micrograph of a bond coat of TiO_2 (center) that adheres very well to the Ti6A14V substrate (left) and to the hydroxyapatite top coat (right). The interface bond coat/hydroxyapatite is continuous even though a crack has developed along this interface, presumably due to stresses introduced during the sample preparation (Heimann, *et al.* 1998). It has been experimentally shown that the adhesion strength of the system titania bond coat/hydroxyapatite coating as measured by a modified peel test (Sexsmith and Troczynski, 1994) increases by 100% compared to a hydroxyapatite coating without a bond coat (42.1 vs. 21.9 N/m) (Kurzweg, *et al.* 1998). A composite titania/ zirconia bond coat increases the peel strength to only 32 N/m (Kurzweg, *et al.* 1998).

(iv) *Materials substitution* through replacement of the coating material hydroxyapatite by bioceramic compositions of the quaternary system CaO-P_2O_5-TiO_2-ZrO_2. These bioactive ceramics show a very high resorption resistance *in vitro* and hence are considered biomaterials with extreme long-term biostability (Szmukler-Moncler, *et al.* 1992; Schneider, 1999). Thermal stability problems exist because decomposition products appear during plasma spraying that may be related to an inherent instability, caused by a high vacancy concentration, of the NASICON (Na-superionic conductivity) structure to which these compositions belong.

Figure 6 shows schematically the various approaches taken by our research group. Figure 6A shows the upper part of the femur with a hip endoprosthesis in place. The Ti6A14V stem carries the ball joint made from either alumina (Figure 1) or stabilized tetragonal zirconia polycrystals (TZP), and is coated with a thin (100-200 μm) plasma-sprayed hydroxyapatite layer. The interfacial region implant/bone is further displayed in Figure 6B. At the immediate interface to the titanium alloy there exists a few nanometer thin layer of native titanium dioxide of variable composition that is partly responsible for the adhesion of the ceramic coating to the metal. Since the metal surface is roughened by grit blasting, the coating locks into surface asperities and thus provides a mostly mechanically dominated adhesion mechanism. Indicated are also the products of thermal decomposition during plasma spraying : oxyapatite $Ca_{10}[(PO_4)_6O]$, tricalcium phosphate $Ca_3(PO_4)_2$, tetracalcium phosphate $Ca_4[O(PO_4)_2]$ and amorphous calcium phosphate ACP (see equations 1-3).

Figure 6C shows the problem that occurs when a gap develops between the implant and the ceramic coating. This has to be overcome by appropriate engineering of either the process, the material, or the design philosophy. Hydroxyapatite bonds very strongly to the bone tissue so that on mechanical failure testing fracturing occurs either in the bone or the implant material but not through the interface (Hench, 1991). This is because hydroxyapatite corresponds in composition and structure to the inorganic component of the composite material "bone". As result of cyclic micromotions by the patient already in the early stages of the healing process, separation can occur and a gap develops into which acellular connective tissue invades.

In Figure 6D, 1-4 the materials engineering approaches described above are schematically displayed. Figure 6D, 1 shows process engineering by optimization of the plasma spray parameters (plasma energy, E varied between 29 and 42 kW; spray distance, x varied between 150 and 360 mm; chamber pressure, P varied between 100 and 200 mbar; powder feed rate varied between 1 and 5 r.p.m., as well as preheating temperature, T). Figure 6D, 2 describes the powder engineering by annealing the as-received hydroxyapatite powder at 1300 °C for 1 hour to reduce the microporosity. Figure 6D, 3 shows the application of a 10-15 μm thick bond coat based on titania and titania zirconia between the titanium alloy substrate and the hydroxyapatite top coat. Finally, Figure 6D, 4 relates to the concept of materials substitution, i.e., hydroxyapatite is being replaced by a highly insoluble calcium titanium zirconium phosphate of NASICON structure, $CaTiZr_3(Po_4)_6$.

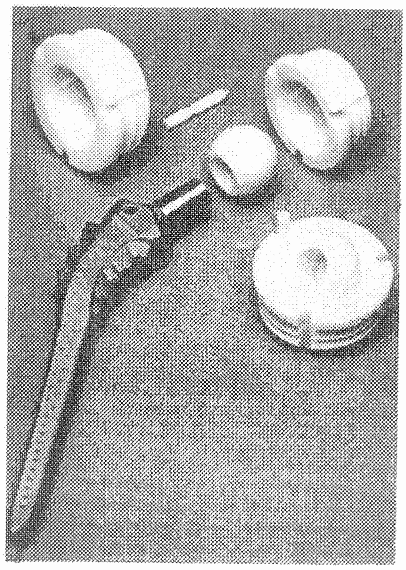

Figure 1 Complete TiA14V hip endoprosthesis with an alumina ball joint and an acetabular cup made from Ti6A14V alloy with an insert of high density polyethylene. (after Hulbert, *et al.* 1987)

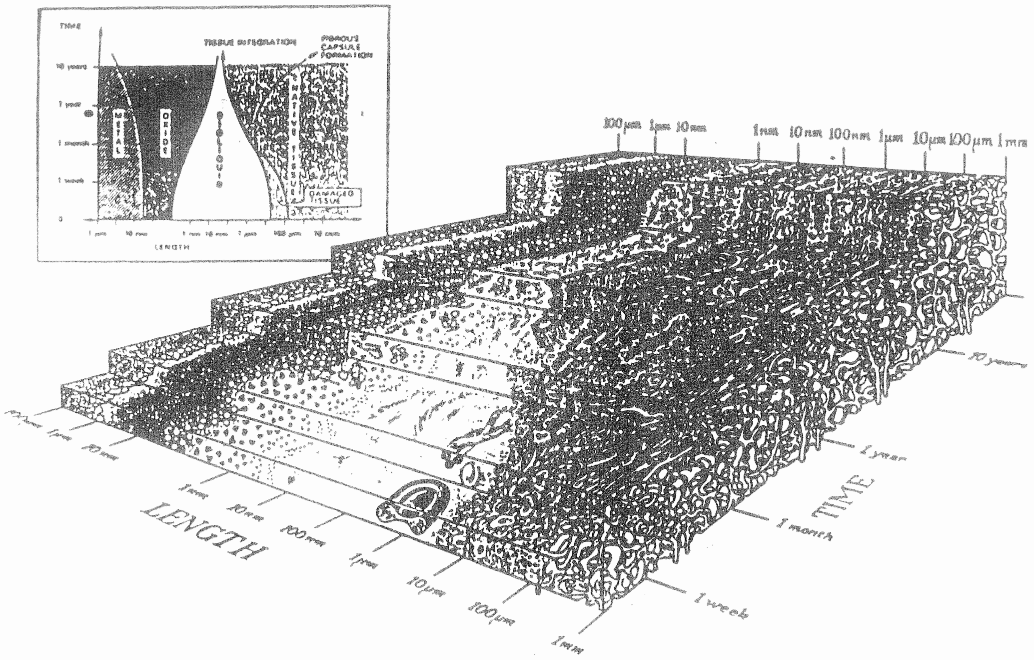

Figure 2 Schematic outline of the interface between the implant (left) and the bone tissue (right), and its dynamic behaviour in time (front to back). The inset shows that implant and bone are initially separated by a fluid layer into which with time bone cells grow. The development of a fibrous capsule at the interface is also indicated. For details see text (after Kasemo and Lausmaa, 1991)

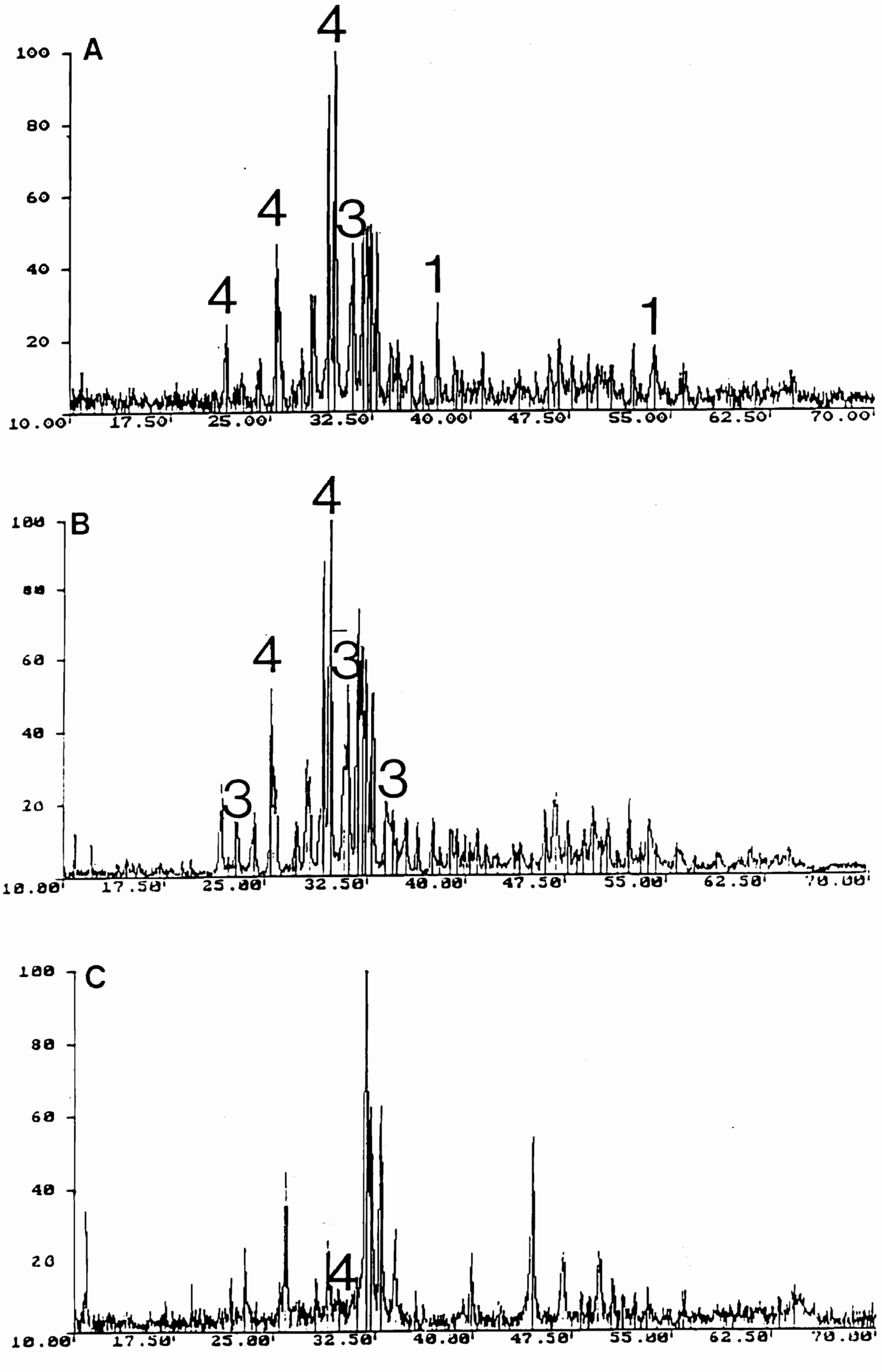

Figure 3 X-ray diffractograms of three hydroxyapatite coatings plasma-sprayed with different parameters.

A : Plasma power 42 kW, chamber pressure 100 mbar, spray distance 240 mm, preheated;

B : Plasma power 42 kW, chamber pressure 100 mbar, spray distance 240 mm, not preheated;

C : Plasma power 42 kW, chamber pressure 100 mbar, spray distance 360 mm, not preheated.

1=CaO, 3=$Ca_3(PO_4)_2$ (TCP),4=$Ca_4[(PO_4)_2O]$ (TetrCP)

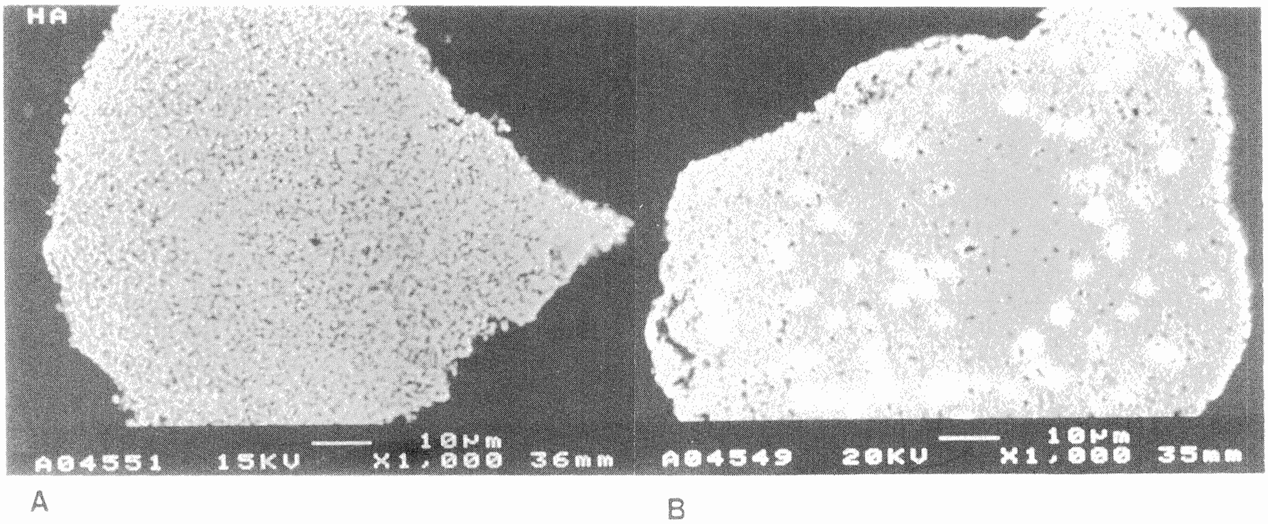

Figure 4 A: Hydroxyapatite grain as-received, showing a high degree of microporosity. B: Hydroxyapatite grain pre-spray annealed at 1300 °C for 1 hour, showing a considerable densification through sintering

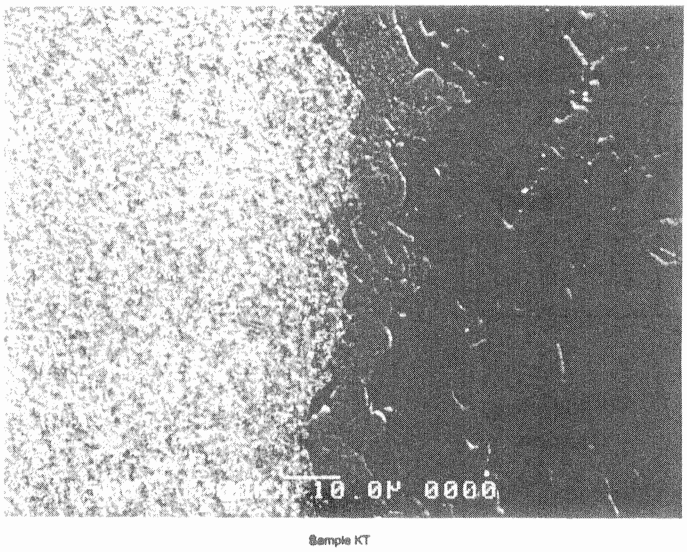

Figure 5 Cross-sectional SEM micrograph showing a titania bond coat (center) that adheres well to both the Ti6A14V alloy substrate (left) and the hydroxyapatite top coat (right). The plasma spray parameters were as follows. Bond coat: Plasma power 42 kW, argon/hydrogen ratio 40:12 l/min, spray distance 80 mm, powder feed rate 20 g/min, traverse speed 30 m/min. Hydroxyapatite: Plasma power 26kW, argon/hydrogen ratio 50:4 l/min, spray distance 100 mm, powder feed rate 24 g/min, traverse speed 30 m/min

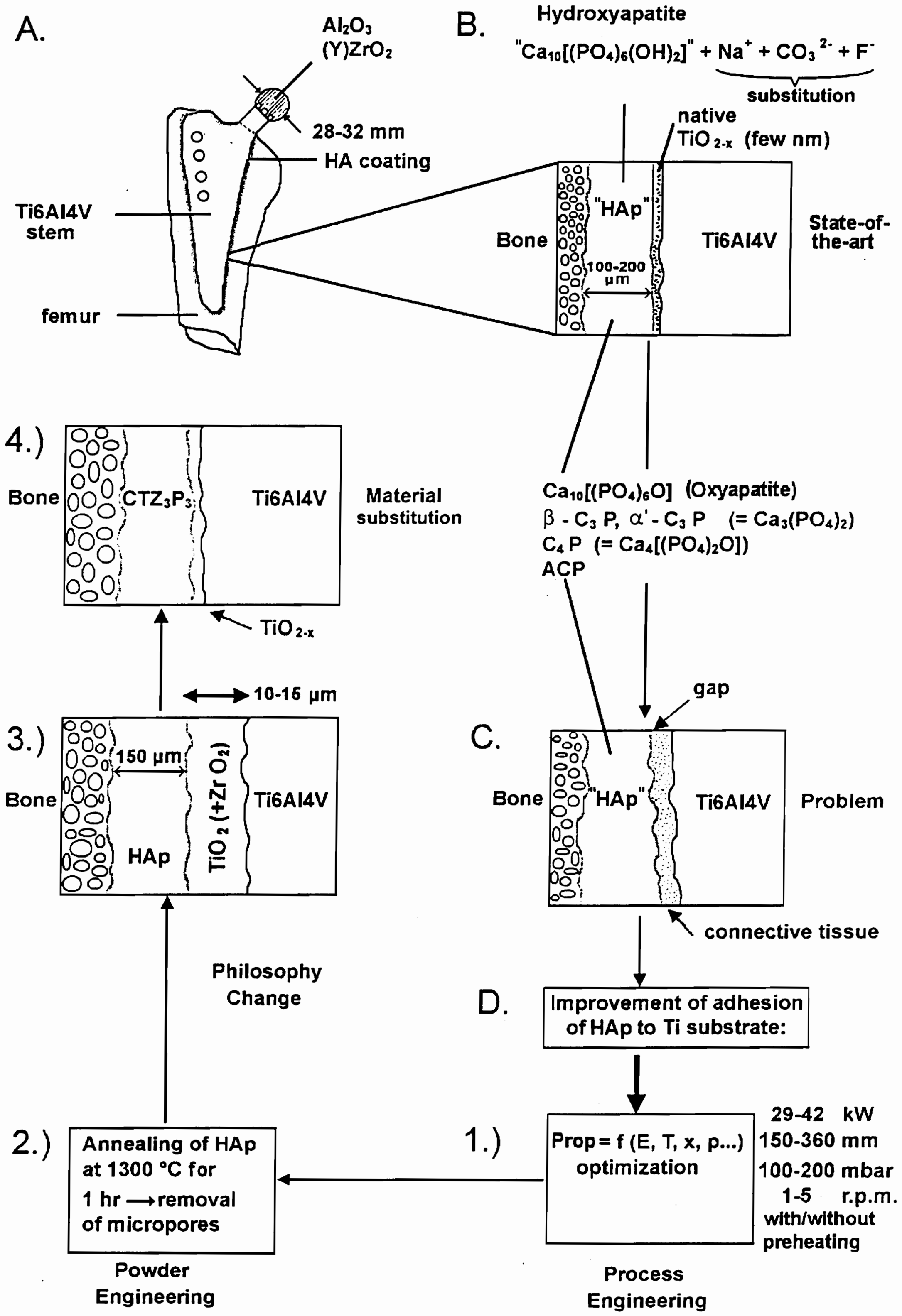

Figure 6 Schematic of different strategies of engineering bioceramic coatings. For details see text

Function of biocompatible bond coats

The utilization of bond coats to increase the adhesion of wear- and corrosion-resistant coatings, as well as thermal barrier coatings, to a given substrate is well documented in the thermal spraying literature (Heimann, 1996). In applications for bioceramic coatings in addition to improving adhesion strength bond coats should also:

(i) prevent direct contact between Ti and hydroxyapatite; such contact is thought to catalyse the thermal transformation of the latter towards tri- or tetracalcium phosphate or even non-biotolerant CaO (Weng, *et al.* 1994; Ji, *et al.* 1992)

(ii) reduce the release of metal ions from the substrate to the surrounding living tissue that, for stainless steel- and cobalt-chrome-based materials, has been shown to induce massive hepatic degeneration in mice (Pereira, *et al.* 1995) and impaired development of human osteoblasts (Tomas, *et al.* 1996)

(iii) reduce the thermal gradients at the substrate/coating interface during plasma spraying. These are caused by rapid quenching of the molten particle splats at the substrate surface that leads to deposition of amorphous calcium phosphate (ACP) with a concurrent decrease in resorption resistance (Heimann, *et al.* 1997) and hence to reduced *in vivo* performance, *i.e.* longevity of the implant,

(iv) prevent a steep gradient in the coefficients of thermal expansion between substrate and coating that promotes the formation of strong residual tensile forces in the coating giving rise to crack generation, chipping and/or delamination, as well as

(v) cushion damage by cracking of the coating and delamination from the substrate initiated by cyclic micromotions of the implant during movement of the patient in the initial phase of the healing process (Soballe, 1993).

Thus it is highly desirable to engineer the substrate/bioceramic coating interface in such a way that by application of a suitable thin biocompatible bond coat layer the advantages addressed above can be realized to help develop a system of total quality assurance for endoprostheses (Faro and Huiskes, 1992). Such a system would constitute a tremendous step forward towards alleviating physical and mental suffering of patients worldwide and saving of a substantial portion of the health costs associated with remediation operations in the event of an implant failure.

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