Review Article

THERMAL SPRAYING FOR BIOCERAMIC APPLICATIONS

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Bioceramics are used in many applications and forms within the human body. Some major shortcomings of bulk ceramics concern their high variability in material properties and restriction to only limited forming operations. However, the excellent biocompatibility of many ceramics has provided a strong incentive to promote investigations for alternative manufacturingprocesses such as ceramic coating technology. Coatings may be applied by pyrolytic deposition, electrophoreticdeposition, sintering, hot isostatic pressing, controlled oxidation, sol-gel techniques, physical vapour deposition (PVD), chemical vapour deposition (CVD), dipping processes and thermal spraying methods. The present work will focus on the thermal spraying of hydroxy-apatite (HAp) onto metallic substrates which are intended for orthopaedic applications. It is intended to present the pertinent literature on HAp as it relates to thermal spraying, and also briefly detail some thermal spraying experiments. The thermophysical processes which occur during thermal spraying will be related to to the structure/property relationshipsof the resultant coating.

1 INTRODUCTION

Materials used for prosthetic applications include polymers, ceramics, metals and composites. The present work is concerned with orthopaedic applications and, therefore, the focus will be directed towards materials that are analogous to the composition of bone. Osseous tissue contains both a calcium phosphate ceramic (hydroxyapatite) and a protein called collagen. Hydroxyapatite (HAp) found in osseous tissue has its structure modified by monovalent and divalent ions such as Na⁺, K, Mg^{2+} , CO_3^{2-} and other ions. The obvious choice for repairing or replacing the supporting structure of the body would be a calcium phosphate ceramic.' Table 1 details some of the ceramics containing calcium and phosphate ions, which are currently used as biomaterials. Some of these materials contain other oxides and form glasses; these ceramics are referred to as 'bioglasses' but should not be confused by a patented ceramic composition which is known as 'Bioglass'. The implant must not only possess chemical compatibility but also good bulk properties and exhibit a strong bond with the

surrounding tissue in applications where they experience high load. Bioglass and HAp are rarely used as stress members in bulk form since their intrinsic strength is poor. Instead they find applications where the mechanical requirements are low (Table 2). It should be noted that ceramics can be designed for a range of applications.

Hench classifies ceramics into three classes which exhibit different reactivities.⁶ Figure 1 shows the relative reactivity of bioresorbable, surface active and inert ceramics. The biodegradation or bioresorption curves can change depending upon the physical and chemical properties of the implant as well as biological relationships between the implant and body. Resorbability can be increased by porosity, reductions in crystal size, more crystal imperfections and smaller grain size. The chemical properties giving rise to the same trend, in HAp ceramics, would be ionic substitutions (for example CO_3^{2-} or Mg^{2+}), the presence of β -whitlockite and impurities. The biological factors include pH drops due to cell-mediated factors (e.g. macrophages, osteoclasts and fibroclasts), osteolytic infection and disease, degree of bone contact, type of bone (e.g. skull, mandible and femur), animal species, age, sex, hormone levels and genetic predisposition.' The time scale for bioresorption and the maximum resorbability within the body can change significantly if all these factors are taken into consideration. Figure 1 adapted from Hench is thus a very simplified picture, which should only be used in pointing out the major distinctions between the three classes of bioceramics.⁶ It should be noted that in vivo assessment of biodegradation includes ascertaining the reduction in implant size, any changes in pH and histomorphometry (measurement of pore size variation). In vitro assessment is much simpler and includes measuring the specimen size and any surface degradation via microscopy.

Inert bioceramics of current interest include alumina, partially stabilized zirconia, titania, silicon

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TABLE 1

Bioceramics containing calcium and/or phosphate ions in their structure

Bioceramic	Chemical composition	Trade names	Reference
Hydroxyapatite (HAp) β -Whitlockite (β -TCP) Tri-calcium phosphate (a-TCP) Tri-sodium phosphate Calcium bydroxide	Ca ₁₀ (PO ₄) ₆ (OH) ₂ β -Ca ₃ (PO ₄) ₂ or 3CaO.P ₂ O ₅ α -Ca ₃ (PO ₄) ₂ Na ₃ PO ₄ Ca(OH) ₂	Durapatite, Calcitite Synthos, Synthograft	2 3,4 5 5
Calcium sulfate Wollastonite Bioactive glass A/W glass ceramic* Bioactive glass ceramic	CaSO ₄ CaO.SiO ₂ Na ₂ O-CaO-P ₂ O ₅ -SiO ₂ system HAp and CaO.SiO ₂ (Na,K) Mg ₃ (AlSi ₃ O ₁₀)F ₂ and HAp crystals	Bioglass	5 2 2 2 2 2
Bioactive glass ceramic Bioactive composites	?	Ceravital Palavital	2 2

* Glass ceramic containing apatite and wollastonite.

TABLE 2

Clinical applications for HAp bioceramics

Application as stress members Artificial joints (i.e. knee, hip, shoulder, elbow, etc) Spinal fusion

Low stress applications Cranioplasty Middle ear implants Tooth implants Alveolar ridge reconstruction (orthognathic surgery) Vascular grafts Percutaneous devices



Fig. 1. Comparison of the relative reactivity of biomaterials (adapted from *Hench*).⁶

nitride, silicon carbide, low temperature isotropic carbon and vitreous carbon. Surface active ceramics include HAp and bioactive glasses while tricalcium phosphate is used for bioresorbable ceramics.'

A ceramic can be tailored to have the properties suitable for each type of implant. One example of this is in fracture healing of bones. The pin used to stabilize fractures will slowly dissolve and weaken if it can be manufactured from an appropriate material. Thus, the bone experiences an increasing load until it is restored to normal loading conditions. This ideal strength-time relationship is illustrated in Fig. 2a:⁹ while Fig. 2b indicates the relationship which may exist for a hip prosthesis in a femur.



Fig. 2 Strength-timerelationship for: (a) tibia with a bone plate⁹ and (b) a femur possessing a hip prosthesis.

The in *vivo* time dependent behaviour of the ceramic depends on the implant material and also the mechanical requirement of the implant by the bone. For instance, a ceramic coated implant performs most effectively where bone cannot regenerate enough to repair any previous damage. The resulting mechanical behaviour of the coated material from the time of implantation would show an insignificant reduction in strength.

The poor mechanical properties of bulk ceramics may be circumvented by using surface reactive ceramics which interface with the biological systems. A coating can be made of this material and the bulk can be made of a tough but less compatible or inert metal that provides mechanical support.¹⁰ The coating is applied to a metallic substrate (commonly Ti-6AI-4V) to enhance the fixation of the implant to the osseous tissue." This coated implant can then take on the characteristics of both metallic and ceramic materials. Results from plasma spraying of HAp show that bone bonding to HAp coatings is essentially the same as to HAp bulk implants.¹² HAp, bioactive glasses and bioactive glass ceramics can develop a bond strength which exceeds the bond strength of metals to bone by a factor of three and the above ceramics are therefore mostly adopted for orthopaedic purposes. The bond strengths of some coating/substrate systems which are attached to bone are reported s

Coating materials	Substrate material	Bond strength (MPa)	Reference
Bioglass 45S5F	Ti alloy	21.1	13
0	316L stainless steel	10.6	13
Ti-6AI-4V	Ti-6AI-4V	5.1-25.5	14
Alumina	Ti allov	23.6	14
	316L stainless steel	26.1	15
Hvdroxvapatite	Ti-6AI-4V	60.0-70.0	16
, , . , . ,	316 stainless steel	8.0	N/A

TABLE 3

Bond strength of biocoatings

in Table 3. It can be noted that the bond strength is variable and depends on, among other factors, the type of bone (cortical or cancellous), the bone thickness and the testing conditions.

HAp has been used to coat Ti-6AI-4V hip implants. The lower part of the stem is cylindrical for ease of bone bed preparation and implant insertion but the shape at the top deviates from a circular cross-section. If the full stem length was cylindrical the implant could rotate and the bone and repaired femur would then experience stresses which were atypical of those that are normally experienced. This could lead to premature implant failure. The coating is applied to the stem because this part interfaces with the osseous tissue and forms a bond joining the implant to the body. The coated prostheses which are commercially available show a difference in design philosophy. The stem can be totally covered with HAp or a section can be left uncoated. The uncoated section would be in the middle of the stem on the back where the implant experiences the least stress.

2 IMPLANT FIXATION AND TI-V-AI ALLOYS

An important reason for applying a coating or modifying the surface is for implant fixation to tissue. This tissue could be bone, a part of an organ, skin or flesh. Orthopaedic applications are concerned with bone bonding so the following fixation mechanisms examine the bonding of the bone to the implant. Each of these techniques (Fig. 3) have evolved separately and are based on different mechanisms. A thermosetting cement such as PMMA is used to adhesively fix the implant in place (Fig. 3a). Disadvantages are cell necrosis from the exothermic reaction and cement failure.17, 18 The reliability of this fixation technique over periods >10 years has been questioned.¹⁹ Despite these shortcomings, PMMA bonding is being improved and it has the advantage of immediate bond formation.20

The second principle involves bone ingrowth into a porous surface (Fig. 3b, c). Either a porous beaded surface or titanium fibre pads are commonly used. In each of these cases the balls or the fibre are



Fig. 3. Fixation methods currently being used for orthopaedic implants (a) bone cement, (b) sintered Co-Cr balls, (c) sintered Ti alloy mesh and (d) ceramic coatings.



Fig. 4. Bonding of HAp implants to bone.

pressure sintered onto the surface to provide a porous surface with the desired pore size for bone ingrowth. Lack of bonding within the porous structure has in the past led to failure.²¹

The method which creates a superior bond to bone is the use of surface active ceramic coatings (Fig. 3d). Osseous tissue grows up to bioglass and HAp coatings and then forms a very intimate bond.²² The mechanism of bone bonding is well documented for Bioglass, but little is known about HAp coated materials. The strength of the bond (~ 60 MPa) lead many to think that bonding could be on the atomic level. An illustration of what is understood about the bonding of HAp to bone is given in Fig. 4. The bonding begins when the implant is covered with a narrow $(3-5 \mu m \text{ wide})$ amorphous electron dense band with no distinct structural details (Fig. 4a). Fissures observed in the amorphous layer (Fig. 4b) suggest that minerals are removed during decalcification. Loosely arranged collagen bundles position themselves between the amorphous zone and cells. Calcification of the amorphous layer occurs (Fig. 4c) with bone mineral crystals depositing in an arrangement that is dependent on the sample preparation technique. As the implant site matures, the bonding zone shrinks to 0.05-0.2 µm between the implant and normal-appearing bone (Fig. 4d). The bonebonding substance on the surface of the implants is very similar in character to natural bone cementing substance and may be characterized as amorphous in structure, heavily mineralized and rich in mucopolysaccharides.23

Note should be made that Ti-6AI-4V is the main substrate material presently in use. The advantages of this alloy are that it is less susceptible to corrosion than other allovs such as 316L stainless steel and Co-Cr alloys, it has a lower elastic modulus and it is less dense and more compatible with the biological system.^{10, 24} It is important that the Ti-6AI-4V alloy has an elastic modulus that is similar to that of bone? If this were not the case then an applied stress in the femur would cause a difference in deformation between the bone and the implant, and this mechanical incompatibility would be transferred to the interface in the form of deformation stresses and strains. Also, a very stiff implant would be subjected to all of the mechanical loading and not allow stress transfer to the surrounding bone. For bone to grow it must be subjected to a stress; otherwise the bone will slowly resorb and the bone front will retreat away from the implant which results, among other factors, in loosening of the prosthesis. The titanium alloy is, at present, the most favoured substrate material of the metallic alloys because its modulus is closest to that of cortical bone (Table 4). It can be noted that the other implant materials show a larger mismatch in the elastic

TABLE 4

Comparison of elastic moduli of current implant materials with that of bone

Material	Elastic modulus (GPa)	Reference
Alumina Co-Cr alloy Mg-PSZ Austenitic stainless steel Ti-6AI-4V HAp Bioglass Pyrolytic carbon Cortical bone PMMA (bone cement) Polyethylene	390 230 205 200 106 100 40-140 24-40 7-30* 4 1	25 25 26 26 26 27 26 25 25 25 25 25

* Modulus is dependent on age of specimen and the region of the body from which it is harvested.

modulus.²⁶ It is important to remember that it is not only the elastic modulus that is of importance since the overall stiffness of the prosthesis can be adjusted by structural design. Therefore, the large discrepancy in the moduli of the prosthesis and bone may be minimized by an appropriate prosthesis geometry.

The modulus mismatch between the HAp (assuming an absence of porosity) and the Ti-6AI-4V substrate is very low and therefore the strain at the coating/substrate interface will be minimized when the prosthesis is stressed. Another aspect of the implant concerns its weight since it is more comfortable for the recipient if the hip is evenly balanced with respect to normal biomechanical activities. Titanium (AI/V) alloys with a density of 4.4 g cm⁻³ would balance a hip more evenly (density of bone is ~ 2 g cm⁻³) than the use of austenitic stainless steel and Co-Cr based alloys which both have densities > 7 g cm⁻³.

3 COATINGS AND SURFACE MODIFICATION

A surface coating can be described as a covering applied to the outer face of an object, whereas surface modification requires a change in the nature of the outer surface. Surface modification has made a significant contribution to the wear resistance, corrosion resistance and fatigue life of titanium alloys. For example, ion implantation has been used to improve the biocompatibility of titanium alloys. An improved tissue attachment to ion implanted surfaces has been reported. This phenomenon is attributed to changes of surface energy which, in turn, affect the wetting of physiological media. The corrosive wear resistance has been improved up to 1000 times.²⁸ Fatigue lifetime is also improved; the degree being dependent upon the choice of ion species.29

A summary of coating processes that have been used to deposit bioceramic materials is given in

Method of application	Coating material	Substrate material	Reference
Electrophoretic deposition	HAp	Titanium alloy	30
Pyrolysis	Carbon	Titanium alloy	31
Hydrólysis	Calcium phosphate	Carbon composite	32
Immersion	Bioglass	Co-Cr alloy	33
Dipping	Bioglass	316L stainless steel	13
	Bioglass	Co-Cr alloy	11
Frit enamelling	НАр	Co-Cr allov	33
Chemical vapour deposition	Carbon	Ti-6AI-4V álloy	34
	TiN-alumina	Stainless steel	35
Physical vapour deposition	TIN	Co-Cr-Mo alloy	36
	Bioglass	Alumina	37
	НАр	Titanium alloy	38
	Carbon	Stainless steel	39
Sintering	Polysulfone	Titanium alloy	· 40
Plasma spraying	HAp	Ti-6AI-4V alloy	22
	Alumina	Ti-6AI-4V alloy	41
	Bioglass	316 stainless steel	13
Hot isostatic pressing	HAp	Titanium alloy	42



Biomaterial coatings and their method of application



Fig. 5. Typical thicknesses of coatings applied by different processes.

Table 5. The coating thickness as seen in Fig. 5, varies from < 1 μ m for sol-gel coatings, to 1-40 μm for PVD and CVD coatings to > 1000 μm for coatings which are produced by thermal spraying, dipping and sintering methods. Coating thickness is an important parameter in bio-applications, since thick coatings tend to crack and fail prematurely due to their greater bending moment. A coating thickness > 100 μ m can potentially introduce fatigue failure under tensile loadings. On the other hand, the coating must be thick enough to avoid dissolution by the physiological solutions. Physiological media will have direct access to the implant-bone interface if the osseous tissue does not interface directly onto the implant; and thereby allow degradation of the implant and hence its loosening. This is especially true when infection occurs because the accompanying fall in pH renders the coating prone to dissolution. There is some dispute in the open literature concerning the optimum thickness of bioceramic coatings which are intended for



Fig. 6. Schematic diagram of the thermal spraying process.

orthopaedic purposes. De Groot has proposed a limitation of 50 μ m whereas Osborn recommends 200 μ m.^{12, 43}

4 THERMAL SPRAY TECHNOLOGY

It is not intended to review the thermal spraying process; however it is useful to summarize some features of the technology which are of special emphasis to the manufacture of bioceramic coatings. Thermally sprayed coatings are produced by injecting particles of 20-120 μ m in diameter into the tail flame of a high temperature source (Fig. 6).44 The source may be either from a d.c. plasma (hence 'plasma spraying'), an oxyacetylene gas mixture ('flame spraying') or an explosive mixture of acetylene, oxygen and nitrogen ('detonation gun spraying'). Table 6 summarizes some of the features of these processes. The underlying principles behind all these processes are similar. Thus, the particles are heated and then driven at velocities of up to 300 m s⁻¹ against a substrate. The molten

TABLE 6	
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Comparison of spraying techniques

Process	Porosity	Advantages	Disadvantages
Flame	10– 15%	Economic	High porosity Prior substrate heat treatment
Arc	10-15%	High deposition rates Greater bond strength than flame spraying	High porosity Prior treatment of substrate
Plasma	1-10%	High bond strength Can use high m.p. materials Inert heat source	Costly
Detonation Gun	0–1%	High hardness Very high bond strength	Costly



Fig. 7. Interdependencies of powder and coating quality (modified from Schwier).47

and semi-molten particles rapidly solidify on impact against the substrate and an integral layer (~ 0.5 -2 mm in thickness) is built up by the overlaying of many particles.⁴⁵ Some droplets may not completely melt before impacting the surface due to particle size, velocity and temperature distributions within the stream of particles and this results in embedded particles in the lamellar structure.

Ceramic coatings are usually not deposited directly onto the substrate due to their brittle nature. It is normal practice for these coatings to be overlaid onto a thermally sprayed metal (which is termed as the 'bond coat') and this acts as a compliant layer between the substrate and the ceramic coating. However, no bond coats are used for HAp coatings on Ti-6AI-4V substrates. The coating adhesion to the substrate as well as the coating integrity is often explained in terms of the mechanical interlocking of the particles when they solidify. When HAp is deposited onto Ti-6AI-4V, a chemical reaction with titanium dioxide (the surface layer of the titanium alloy) at 1000°C forms CaTiO₃ and tricalcium phosphate.¹⁶ The CaTiO₃, a compound formed from both the substrate and the HAp coating, acts as a bond layer. The formation of an interfacial compound is not unique to the plasma spraying process since this also occurs with electrophoretic coatings.⁴⁶ Thus, the adhesion of HAp to Ti alloys is much stronger (– 60 MPa) than bonding mechanisms, which rely on only mechanical interlocking. It is important to point out that the plasma spraying process can be carried out under either ambient or low pressure conditions.⁴⁴ Low pressure plasma spraying (LPPS) is carried out at – 6 kPa and gives rise to very dense coatings with high adhesion strengths.

The quality of thermal spray coatings is a complex problem since there are various interdependencies (Fig. 7) between powder properties, the spray process and coating quality.⁴⁷ Thermophysical properties are determined by the particle morphology and their composition. Melting behaviour is influenced by particle size, thermal conductivity, melting point, purity and spraying parameters. The deposition of the molten particles and the final coating quality are determined by the spray parameters such as the spray rate, gas type, gas flow, spraying distance and nature of the substrate. All stages of the plasma spraying process are thus affected by the characteristics and the properties of the powder.

Transport during the thermal spraving operation and subsequent powder properties which affect its deposition onto a substrate are: bulk density, particle shape, particle size, percentage of superfines (< 10 μ m), particle surface smoothness, hydroscopic density (moisturepick-up), chemical stability and electrostatic charging effects (which may produce particle clumping). Spherical powders of a given size distribution are important as they give consistent melting behaviour which increases deposit efficiency. A uniform surface area ensures consistent melting but the melting characteristics become erratic when the surface area, particle dimensions and mass for similarly sized powders vary.48 The optimum particle shape from the viewpoint of flow characteristics is spherical since then the best aerodynamic performance is achieved. The flight path of a particle that deviates from sphericity will be more unpredictable.



Fig. 8. Adherence decrease of plasma sprayed alumina on Ti-6AI-4V after ageing in saline *solution*.⁵¹

The thermal spraying technique is widely documented for bioceramic applications and was pioneered for biomaterial applications by Brown in the early 1980s. It was established that alumina coatings in the y-phase developed a bond strength of = 25 MPa.¹⁰ There is, however, concern that plasma sprayed alumina exhibits questionable biocompatibility because it reacts more readily with physiological environments than its fused, sintered or hot pressed counterparts. Aluminium ions are released and form bayerite (Al₂O₃·3H₂O) and other compounds which have led to renal failure during animal tests.^{49, 50} The bond strength of alumina coatings decreases when they are aged in physiological media (Fig. 8). For example, the adhesion of plasmasprayed alumina on a 316L stainless steel substrate is lowered from 34.5 to 10.3 MPa after ageingin a physiological medium (Medium 199) for 16 weeks.⁵¹ There is an initial rapid decrease in strength to 13.8 MPa within 8 weeks. Any further loss in strength occurs at a much lower rate.

The plasma spraying of HAp was first documented in the open literature by De Groot in the 1980s.¹⁶ This method is now being used by 'Joint Replacement Instrumentation' based in London, England to coat the femoral stem of 'The Furlong' HAC Coated THR (total hip replacement) system'.⁵² The surface of the femoral stem of the hip implant is plasma sprayed to a thickness of > 200 μ m and can then be pressure-inserted into a cavity slightly smaller than the implant to provide a no-motion fit with the surrounding bone. Within a week the osseous tissue begins to grow onto the surface of the HAp coating to provide a functional interface that can transfer stress.⁴³

5 POWDER PRODUCTION AND COATING MANUFACTURE

The calcium phosphate system although _{CO}n_ ceptually simple displays a rich and complex

Source	Name*	Ca/P ratio [†]	Surface area (m ² g)	Reference
Asahi Optical Co. Euro Crystals Fischer Scientific Fluka Mallincrodt Corp Merck Monash University NGK Spark Plug Co. Plasma Biotal Ltd. Podmore Sigma Trans-Tech, Inc.	Apaceram Hy-Apatite HAp High resolution HAp HAp HAp HAp XVC-56 Calcined bone ash Calcium phosphate HAp	 1.66 1.55 1.62 1.77 	40 	N/A N/A 22 53 54 30 N/A 55 56 57 58 N/A
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TABLE 7 Sources of HAp powder

* Terminology used by manufacturer.

† The ideal ratio according to the stoichiometry of HAp is 1.67.

TABLE 8	

Processes available for the production of HAp

Process	Reactants	Reference
Hydrolysis	Ca₀(PO₄)₀H(OH) Ca₄(PO₄)₂O	60 60
Hydrothermalsynthesis	CaaH2(PO4)25H2O Ca(CH3COO)2:H2O & (C2H5O)3PO Ca(NO3)2 & (NH4)2HPO4 CaHPO, H2O4 & CAHPO, 2H2O	61 62 63
Hydrothermalexchange Solid process Sol-gel Spray pyrolysis Wet method	CaHPO ₄ , H ₃ PO ₄ & CaHPO ₄ :2H ₂ O CaCO ₃ & (NH ₄) ₂ HPO ₄ with H2O Bovine bone Calcium and phosphorus alkoxides Ca(NO ₃) ₂ & H ₃ PO ₄ in Me-H ₂ O-HNO ₃ CaCl ₂ · 6H ₂ O & (NH ₄) ₂ HPO ₄ CaCl ₂ & Na ₂ HPO ₄ CaCl ₂ & M ₃ PO ₄ Ca(NO ₃) ₂ · 4H ₂ O & (NH ₄) ₂ HPO ₄ Ca(NO ₃) ₂ · 4H ₂ O & (NH ₄) ₂ HPO ₄ CaCO ₃ , CaO, Ca(OH) ₂ , CaF ₂ , CaCl ₂ , Ca(NO ₃) ₂ Wor CaC ₂ O ₄ powder with H ₃ PO ₄ solution Ca(NO ₃) ₂ & Na ₂ HPO ₄	64 65, 66 67 68 69 70 71, 72 64 73 74 23 75
	Ca ₃ (Γ Ca ₁₂ & Π_2 U Ca(OC ₂ H ₅) ₂ -EtOH & H ₃ PO ₄ -EtOH CaO (or Ca(OH) ₂) & CaHPO ₄ ·2H ₂ O CaHPO ₄ ·2H ₂ O & CaCO ₃ Ca(CH ₃ COO) ₂ & (C ₂ H ₅ O) ₃ PO Ca(NO ₃) ₂ & (NH ₄) ₂ PO ₄ Ca(OH) ₂ & H ₃ PO ₄	76 77 78 79 80 81-86

TABLE 9

Dependence of morphology on the production process of HAp

Process	Morphology	Reference
Hydrothermal synthesis	Hexagonal-prism Needle-like prisms or spherical particles	63 62
Hydrothermal exchange	Variable	65
Spray pyrolysis Wet method/freeze drving	Spherical Plate-like	69 79
Wet method	Plate-like	71
	Jagged/spherical	86

TABLE 10

The Ca/P ratio of some calcium phosphates

Calcium phosphate	Name	Ca/P ratio
Ca(H ₂ PO ₄) ₂ CaHPO ₄ ·2H ₂ O CaHPO ₄ Ca ₂ P ₂ O ₇ Ca ₄ (PO ₄) ₃ H.3H ₂ O β-Ca ₃ (PO ₄) ₂ α -Ca ₃ (PO ₄) ₂ Ca ₁₀ (PO ₄) ₆ (OH) ₂ Ca ₄ P ₂ O ₈	Brushite Monetite Pyrophosphate Octacalcium phosphate Whitlockite a-tricalcium phosphate Hydroxyapatite Tetracalcium phosphate	0.5 1.0 1.0 1.3 1.5 1.5 1.7 2.0

thermal chemistry.²³ The choices of reaction routes are many; each having reactants and conditions unique to the process. Sources of HAp powders are detailed in Table 7. There are a total of seven HAp production routes documented in the literature. They include hydrolysis of calcium phosphates, hydrothermal synthesis, hydrothermal exchange, solid-processes, spray pyrolysis, sol-gel and the wet method. The most commonly used technique is the wet method (Table 8), and this allows a more extensive choice of reactants compared with the other processes.

Variations in these routes lead to differences in morphology (Table 9), crystallographic structure, stoichiometry and density. In the wet process a difference in composition could arise from HPO₄²⁻ or H₂O that have a tendency to adhere to the particles.^{87, 88} The density depends on the stacking of the separate crystals. The individual crystals are aligned more efficiently thus imparting a higher density to the powder. A process should be chosen to obtain the powder with the desired characteristics. The overall density of the HAp is determined by the stacking efficiency of the individual

HAp crystals; so that a higher density will arise from efficient packing.

The powders used in the present study were prepared by the wet method that has been described by Aoki et al.⁸⁹ This method involves the addition of an acid (orthophosphoric acid) to a base (calcium hydroxide). It is important that the reactants have the correct molar ratio of calcium and phosphorus. Low pH conditions yield more stoichiometric precipitates, but as the pH increases less stoichiometric precipitates are formed.⁹⁰ In the case of HAp, the pH is greater than a value of 8 for the reaction. Careful monitoring of the pH level can be omitted if the reactants contain calcium and phosphorus in a molar ratio of 1.67 and the solution is well mixed during the course of the reaction. A lower Ca/P ratio corresponds to a lower pH and leads to the production of calcium monophosphate and calcium phosphate dihydrate. These materials, whose formulas are shown in Table 10, are soluble in aqueous media and will resorb upon implantation. Both monetite and brushite formation is favoured by insufficient mixing of the calcium containing solution as the PO_4^{3-} solution is added. The PO_4^{3-} ion concentration builds up when it is not distributed homogeneously and a localized low pH is established. This part of the reaction vessel is richer in PO_4^{3-} and provides conditions for the formation of soluble precipitates.

Most wet methods entail adding the phosphate solution dropwise to the calcium ion containing solution. The reason for this is that precipitated anions ($PO_4^{3^-}$) are generated slowly in solutions containing the metal ion (Ca^{2^+}) to be precipitated. This is controlled by hydrolysis of suitable compounds under the condition for formation of insoluble HAp.

The resulting gelatinous precipitate is allowed to settle and the clear liquid decanted. Crystal size is $< 1 \,\mu m^{91}$ but due to flocculation the crystals form aggregates $\sim 20 \ \mu m$ in size. The size distribution of particles can be varied by altering the reaction conditions and, for instance, a larger particle size results when the addition rate of the acid is lowered. The temperature is allowed to settle to room temperature after the reaction reaches completion and the precipitate is left in the mother solution overnight. Water can be evaporated by oven drying at 180°C for 36 h. This removes any absorbed water from the external surface but is insufficient to remove water from ultrafine pores in the particles.92 This water is removed during the calcining stage. The HAp cake is usually processed by crushing, arinding and sieving to the required particle size of 25-185 pm.

Particles produced were of a roughly spherical morphology. At longer drying times (48h) the caked materials had a lower moisture content and the resultant particle agglomerates were therefore harder. Thus these materials, upon crushing, produced a more angular surface morphology (Fig. 9). The resulting powder was identified as amorphous HAp using X-ray diffraction. After calcining at 800° C for 3 h the peak width decreased and the peak height increased more than two-fold to 1500 ct/s as shown in Fig. 10. This behaviour is characteristic for a powder which has become crystalline. The three major peaks indicated in Fig. 10 are located at 28 values of 31.8, 32.3 and 32.9 and have relative intensities of 1, 0.6 and 0.6 respectively.93 Both crystallinity and purity of the source HAp powder are important for the development of a pure crystalline coating.⁹⁴ It is believed that an amorphous coating



Fig. 9. HAp particle morphology after: (a) a long drying time and (b) a short drying time.



Fig. 10. XRD trace of HAp.

will be resorbed by the body and thus a crystalline form is most preferable.

HAp plasma sprayed under ambient conditions partially transforms to tricalcium phosphate and calcium oxide. This transformation can be avoided by keeping the plasma gas at a low hydrogen/argon ratio during the plasma spraving process.⁹⁵ A low pressure plasma spraying facility was also used to apply coatings 100 μm thick. Particle sizes from 25-185 μ m were used but only the particles < 50 μ m in diameter were totally molten (Fig. 11). To assist the melting of HAp the pressure could be raised giving more dense, better formed coatings. Incomplete melting could also be observed if the chamber pressure was too low. It was easier to melt the HAp by plasma spraying under ambient conditions; presumably because the heat transfer from the plasma effluent to the particles under vacuum conditions is quite poor.

The phases which may form upon heating include tricalcium phosphate and tetracalcium phosphate. Whitlockite (i.e. tricalcium phosphate of the beta phase) forms at 1200°C but with HPO₄²⁻ it is known to transform at lower temperatures.⁹⁶ At temperatures > 1400°C a phase transformation from the β -phase occurs and tetracalcium phosphate forms. These transformations have been reported in the plasma spraying process and might appear as a

hindrance to the performance of the coating but both tricalcium phosphate and tetracalcium phosphate may transform to HAp through hydrolysis upon implantation in the human body.

The transformation is accompanied by a volume change. For example, the crystal structure changes from orthorhombic (a-tricalciumphosphate) to hexagonal (HAp) which not only increases the packing efficiency of atoms but also leads to a decrease in the unit cell volume. The manner by which this transformation influences the prosthesis fixation has not been established.

6 CONCLUDING REMARKS

The purpose of the present review has been to outline the chemistry, processing schedules and properties of HAp materials which are intended for bioengineering applications. The focus has been on powder processing methods that enable materials of the appropriate chemistry, particle size and particle distribution to be manufactured. Such powders could be used for bulk ceramic processing operations (e.g. pressing and sintering, etc) or to enable coating processes. The current experimental work established that powders suitable for thermal spraying must be of approximately spherical morphology, with a particle size from $\sim 20-100 \,\mu m$



Fig. 11. Plasma sprayed HAp: (a) under ambient conditions and (b) under low pressure conditions.

and a mean particle size of \sim 55 μ m. Powders of this specification have been successfully plasma sprayed under ambient and low pressure conditions. No high quality deposits, as distinguished by good adhesion to the substrate and internal coating integrity, are formed by flame spraying of the HAp.

The thermally sprayed deposits showed a range of morphologies. The particles were either wellmelted and formed an integral part of the coating or were only partially melted and exhibited many high profile surface features. The partially melted coating would also be expected to exhibit a higher degree of bulk porosity as well as larger sized porosity. This, is an important microstructural feature of the coating to ascertain since the nature of any porosity will determine the ingrowth rate of bone tissue into the ceramic coating. It should also be emphasized that relatively low mechanical properties of the coatings may not limit the utility of the coating to a high degree, as they would in usual engineering applications. Thus, the usual requirement of obtaining dense and highly adherent coatings may, to a certain extent, be of less importance than the need to control the pore size and pore network so that any tissue/implant interactions are optimized.

The processing technology that has been most widely documented is that of atmospheric pressure plasma spraying. It can be noted that traditional thinking would propose that ceramics cannot benefit from LPPS since ceramics generally exhibit high melting points and are therefore relatively stable to thermal treatments. Thus, LPPS technology is normally restricted to the production of high density coatings of reactive metals (e.g. titanium and nickel-chrome alloys). However, the present work indicates that some thermal reduction of slightly impure HAp materials may be minimized by spraying under LPPS conditions. It was also established that coatings of HAp could be manufactured with powders of finer particle size by employing LPPS technology. The implication of these results is that the character of the porosity may be controlled by using a finer cut of powder in conjunction with LPPS technology.

It is important to make some comments with regard to the mechanical properties of thermally sprayed coatings. Data has been reported on bond strengths in the range of 60-70 MPa for HAP coating ~. It-can be noted that such large values are quite uncharacteristic for thermally sprayed ceramics. For example, alumina and zirconia coatings which are intended for aerospace applications, have recommended strengths of \sim 45 MPa. An additional fact is that these aerospace coatings are normally used in conjunction with a bond coat whereas no mention of a bond coat is made for the HAp materials. Thus, it seems that the presently used bioceramic coatings may be over designed with respect to their intended use, and that the enhancement of this material property might give something other than the most preferred microstructure of the coating.

It has also been emphasized that HAp coatings are not used in conjunction with a bond coat. Bond coats of Ti and Ni-Al alloys are normally used to improve the adhesion of the coating system onto the substrate. However, very high strength values are reported in the literature for HAp materials and it has been postulated that highly adherent oxide layers at the substrate surface promote this high adhesion. It can be further noted that there has been little work with regard to determining the

behaviour of coatings with respect to their fracture toughness, fracture morphology and fracture mechanisms under environmental conditions. Another important material property which has not been ascertained is the elastic modulus of the coating. Such measurements would enable a database to be established so that modelling of the coating behaviour could be performed.

It can be concluded that it is crucial to establish the above material properties; and, for example, examine the mechanism whereby porosity improves the tissue ingrowth prospects of the implant, yet also reduces the adhesion and toughness of the material system. It is necessary to perform a reproducible test which simulates the stress and/or environmental conditions under which the coating is subjected to during its service life. It is only by ascertaining such processing/structure/materials property relationships that these bioceramic materials can be further developed.

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