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Characterization of Thermal Sprayed Hydroxyapatite Powders and Coatings

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Calcium phosphate materials such as hydroxyapatite (HA) have biocompatible properties that can promote osteogenesis or new bone formation. Thermal spraying is an economical and effective process for coating the hydroxyapatite onto metal. It has been reported that plasma spraying changes the degree of crystallinity as well as the phase composition of the HA. This article reports the preparation and characterization of HA powders and coatings by two thermal spray processes (plasma and combustion flame) and suggests that the state of the starting powder adversely affects the coating characteristics. The raw HA powders are synthesized through a chemical reaction involving calcium hydroxide and orthophosphoric acid. Phase analysis using an X-ray diffractometer revealed that the synthesized powder consists of predominantly the HA phase. Calcined and crushed HA powders of various size ranges were fed into the plasma jet to produce HA coatings on metallic substrates. In addition, some HA powders were sprayed into distilled water by plasma spraying and combustion flame spraying to study powder melting characteristics. Other samples were plasma sprayed onto a solid rotating target to study atomization and impact behavior. The morphology of the rapidly solidified powders and thermal sprayed coatings were examined by scanning electron microscopy (SEM). An X-ray sedimentation particle size analyzer, laser diffraction particle size analyzer, and image analyzer performed the particle size analysis. Preliminary results indicate that particle cohesion, size range, and thermal treatment in the plasma affect the phase and structure of the as-sprayed coating, and some post-spray treatment may be necessary to produce a dense and adherent coating with the desired biocompatible properties.

1. Introduction

HYDROXYAPATITE (HA) is a bioceramic with unique bioactive properties that make it suitable for bone substitution and bio-interfacing in surgical implants. It has a mineral constituent similar to bone. The high Ca/P-rich environment at the HA surface favors tissue response by accelerating and enhancing fixation to hard bone without the interaction of soft tissues.[1,2] This desirable surface-active characteristic, which promotes intimate bone in-growth by biological fixation, is not observed with the other classes of bioinert materials.

This unique behavior is essential in the development of the cementless joint for total hip replacement (THR), which relies on the speedy and extensive formation of a strong biological bond (similar to those formed on HA implants) that cannot be broken without the fracturing of surrounding tissues.[3]

In addition to other properties such as low thermal and electrical conductivity and elastic properties compatible with bone,[4] HA has the ability to control the degradation rate by altering the material characteristic,[5] which is an important engineering advantage in the development of new biomaterials.

Dense HA, $Ca_{10}(PO_4)_6(OH)_2$, is essentially nonresorbable and suffers little or no biodegradation after a 6-month implantation period.[6] However, the resorption behavior can change if chemical, structural, and compositional aspects of the apatites present differ from those of dense HA.

Although stoichiometric HA has the exact Ca/P ratio of 1.67, other calcium phosphate compounds exhibiting Ca/P ratios in the range 1.5 to 1.67 have been reported[5,7] to exhibit favorable biological response. This tolerance in compositional variation is not too surprising because natural HA in bone is nonstoichiometric as well.[8]

The structure of HA has an effect on biological response. The resorption behaviors of dense and porous HA are clearly different. A dual-phase structure having a higher proportion of a resorbable phase like tricalcium phosphate (TCP) is likely to lose structural integrity at a faster rate than a single-phase HA structure. These effects suggest that biological behavior is sensitive to phase composition and microstructure.

There still exist some apparent inconsistencies in the performance of HA. Although most studies have shown HA to improve interfacial bonding as a result of rapid and extensive bone in-growth,[9-11] others have observed HA-coated implants to perform similarly to metallic implants.[12,13] The inconsistencies in the reported tissue responses may be attributed to biological sensitivity to microstructure, quite possibly from process-induced changes that can cause physical and chemical modification of the starting material. This modification can certainly be expected in thermal spraying where the coating and the starting material are known to differ in phase composition and microstructure.

This study examines the phase changes in HA powders and coatings after thermal spraying and attempts to relate these changes (such as amount of crystalline and amorphous phases) to effects of particle size and melting behavior in the hot jets.

Key Words: agglomeration, feedstock, hydroxyapatite, powder morphology, spheroidization, x-ray diffraction

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Table 1 Operating parameters for dc plasma spraying

Plasma torch	
Model	SG 100, 40 kW
Anode	Backward injection (165)
Cathode	Subsonic mode (129)
Powder	800 A, 32 V
Primary gas	Argon
Secondary gas	Helium
Powder feeder	
Wheel	Fine powder type
Feed gas	Argon
Feed rate	15 to 20 g/min

2. Experimental Procedure

2.1 *Powder Production*

HA powder was prepared using the wet method by reacting $0.28M$ orthophosphoric acid with $0.5M$ calcium hydroxide.[14] This formed a gelatinous precipitate that was separated by decanting the excess water and subsequently drying in an oven at 180 °C until a solid cake remained. This precipitate was further processed by calcination (800 °C/4 h) and subsequent crushing and sieving to achieve two particle size ranges suitable for plasma spraying (56 to 75 and 75 to 106 μm).

2.2 *Thermal Spraying*

The calcined HA was sprayed with a 40-kW plasma torch (SG-100 from Miller Thermal, Inc., Appleton, WI) using Ar/He as the plasma-forming gases. Combustion flame spraying (Miller FP 73) using oxygen and acetylene as combustion gases was also carried out on similar calcined HA. In both cases, a computerized closed loop controlled powder feed hopper was used to ensure accurate powder delivery. The plasma spray parameters are listed in Table 1.

2.3 *Particle Spheroidization*

Spherical particles were produced by plasma spraying into a tank of distilled water. The plasma torch was directed at an angle of about 70° to the water surface at a distance of 35 cm (14 in).

2.4 *Plasma Melt and Rapid Solidification*

The plasma melt and rapid solidification (PMRS) method consists of a direct current (DC) plasma spray system and a double-sided stainless steel wall chamber that houses the rotating substrate. The driving mechanism for the rotating substrate is mounted on top of the chamber while the plasma gun is fixed onto a steel bar holder welded to the bottom of the base plate of the chamber. A detailed description of the powder production system is reported in an earlier work.[15]

2.5 *Phase Identification*

The Philips MPD 1880 diffractometer system was used for phase identification. The operating parameters were CuKα radiation (45 kV/30 mA), divergence slit of 1°, receiving slit width of 0.1 mm and a 2θ scan rate of 1 degree/min.

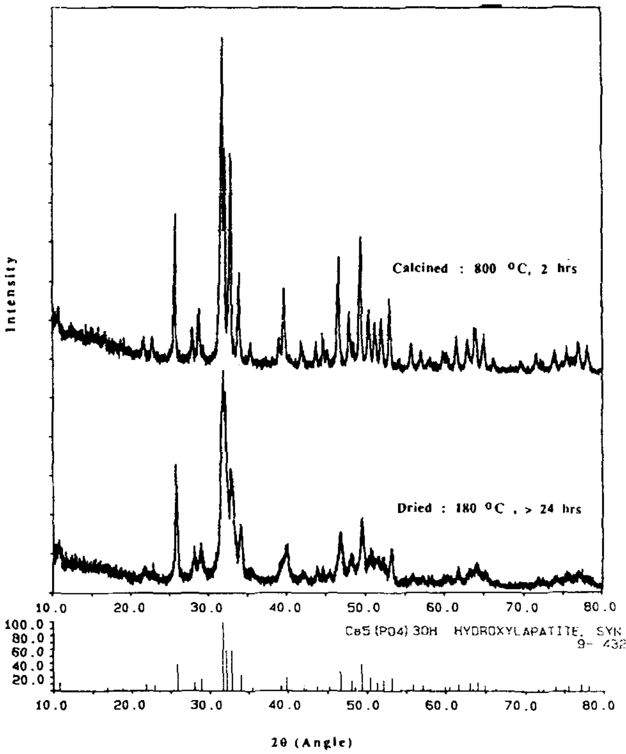

Fig. 1 XRD spectra of as-prepared and calcined HA powders

2.6 *Particle Size Analysis*

Three techniques were used to determine the particle size distribution of the particles. The X-ray sedimentation technique (Sedigraph Model 5100, Micromeritics, Norcross, GA) measures the adsorption of X-rays from a dispersion of particles in a liquid suspension. The laser diffraction technique (Fritsch Analysette 22, from Fritsch GmbH, Germany) measures the particle size through Fraunhoffer diffraction of light from a He-Ne laser source by dispersed particles traversing the collimated light beam. The third technique utilized the combination of a polarizing light microscope and the Quantimet 520+ image analyzer by Leica that discriminates and measures particle sizes based on gray level differences.

2.7 *Particle Morphology*

The Cambridge 360 scanning electron microscope was used to study the surface characteristics of both coatings and particles. The amorphous phases in the particles were determined using XRD and polarizing light microscopy.

3. Results

XRD analysis of the as-prepared and calcined powders revealed essentially pure crystalline HA (Fig. 1). The calcined powders showed much narrower peaks and higher peak intensities, indicating crystal growth and an increased proportion of the crystalline phase. An XRD spectrum of an as-sprayed coating (using 75 to 106 μm powder) is shown in Fig. 2. Several features can be observed in this spectrum that differ from those of the cal-

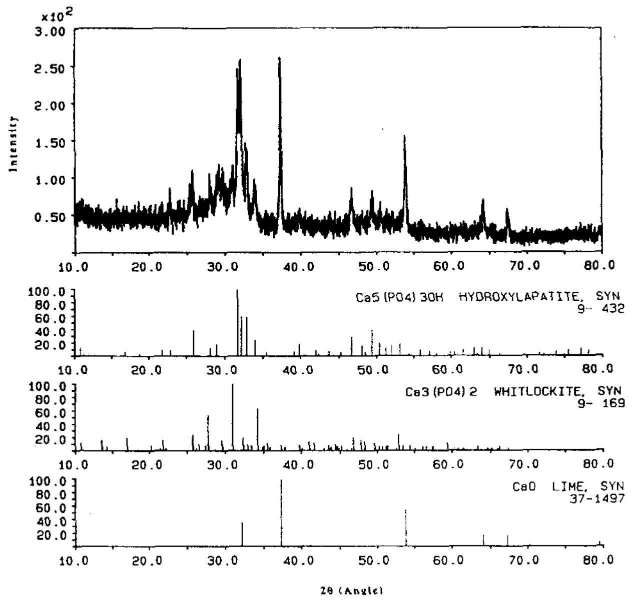

Fig. 2 XRD spectrum of plasma-sprayed HA coating

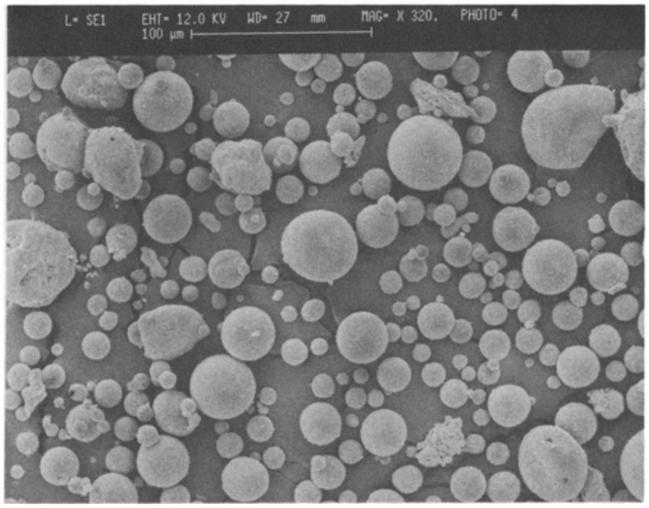

Fig. 3 SEM image of plasma spheroidized HA

cined starting material: the reduction in the peak intensity of HA, the appearance of other phases like TCP and CaO, and the formation of amorphous calcium phosphate (as indicated by peak broadening).

The SEM photomicrograph and particle size distribution of the plasma spheroidized HA powder are shown in Fig. 3 and 4. This powder was produced from a batch of calcined 56 to 75 µm. Fragmentation of the calcined particles was apparent from the range of smaller particles collected. Under these spraying conditions, the largest spherical particle observed was approximately 55 µm. Plasma sprayed HA from the original size range 75 to 106 µm contained more unmelted particles. However, the largest spherical particle observed was similar in size to the largest obtained from the 56 to 75 µm powders. A bimodal distribution of spheroidized particles was also evident (Fig. 4). On the other hand, flame sprayed HA powder exhibited a narrower, unimodal particle size distribution (Fig. 5).

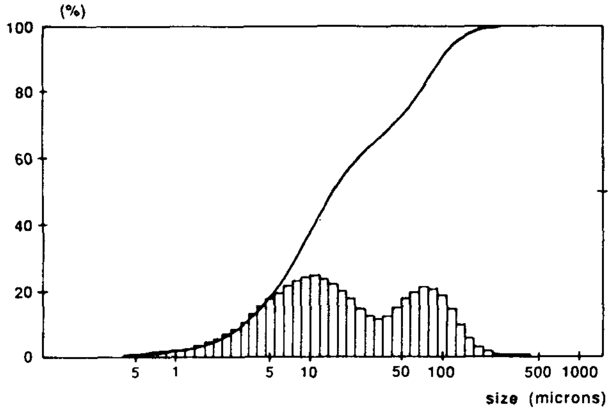

Fig. 4 Particle size distribution of plasma spheroidized particles from 56 to 75 µm agglomerated powder measured using the laser diffraction technique

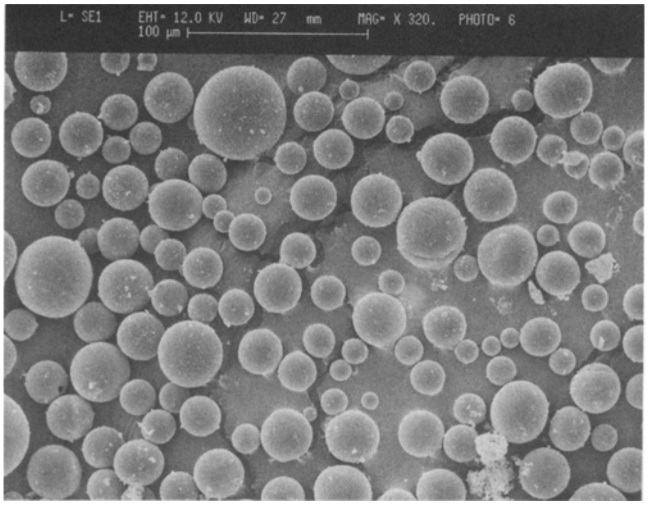

Fig. 5 SEM micrograph of flame spheroidized HA

The XRD analysis of three size ranges of plasma spheroidized powder is shown in Fig. 6. Each range has a different degree of crystallinity and phase composition. The crystallinity of HA decreases with decreasing size. There were small traces of TCP in the three size ranges. Only particle sizes less than 20 µm have CaO present. Heat treatment was found to restore the crystallinity of the thermal sprayed powders (Fig. 7). The XRD analysis showed that (211) peak intensity of plasma-sprayed HA powders in the size range 10 to 20 µm increased threefold after treatment at 600 °C for 1 h and fourfold at 800 °C for 1 h.

The proportion of amorphous calcium phosphate in various particle size ranges was confirmed by polarizing light microscopy. Under cross-polarizers, the crystalline particles show color changes with orientation and periodically cycle between extinction and diagonal positions because of their birefringent characteristic. These were essentially large, unmelted angular particles that were above 75 µm. On the other hand, fully melted spherical particles <30 µm were optically transparent and therefore amorphous. However, there were some particles that were both transparent as well as crystalline. They have amorphous outer layers as a result of partial melting and the crystalline inner structure of agglomerated crystallites.

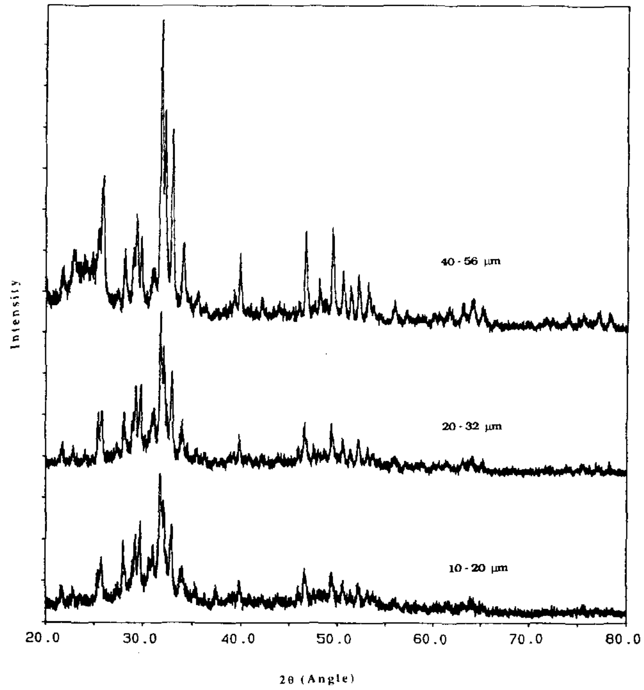

Fig. 6 XRD spectra of spheroidized particles of different sizes

Particle size analysis using X-ray sedimentation showed that the particle size range of the as-prepared HA precipitate was about 2 to 4 µm (Fig. 8). Thus, the larger HA particles were agglomerations of these fine particles, with bond strength between fine particles totally dependent on the drying and calcination conditions.

Powder feedstock with an initial size <106 µm was injected into the plasma jet and propelled at high velocity onto a nonwetting surface. There, the stream of molten droplets disintegrated into many finer droplets on impact with the rotating disc. This is an effective technique in converting coarse agglomerated feedstock into finer spherical particles. Many of the product particles were less than 20 µm.

The SEM observation of HA coatings prepared from calcined HA powders in the size range 56 to 75 µm showed a variety of features. Among these were open surface pores, cracks, smooth splats, and very fine scale deposits (Fig. 9). Apart from the fully melted structures, partially melted and spheroidized particles were also observed to adhere to the melted layers.

4. Discussion

Coatings that were produced from uncalcined 75 to 106 µm and calcined 56 to 75 µm powders contained various phases: crystalline HA, TCP, CaO, and amorphous calcium phosphate.

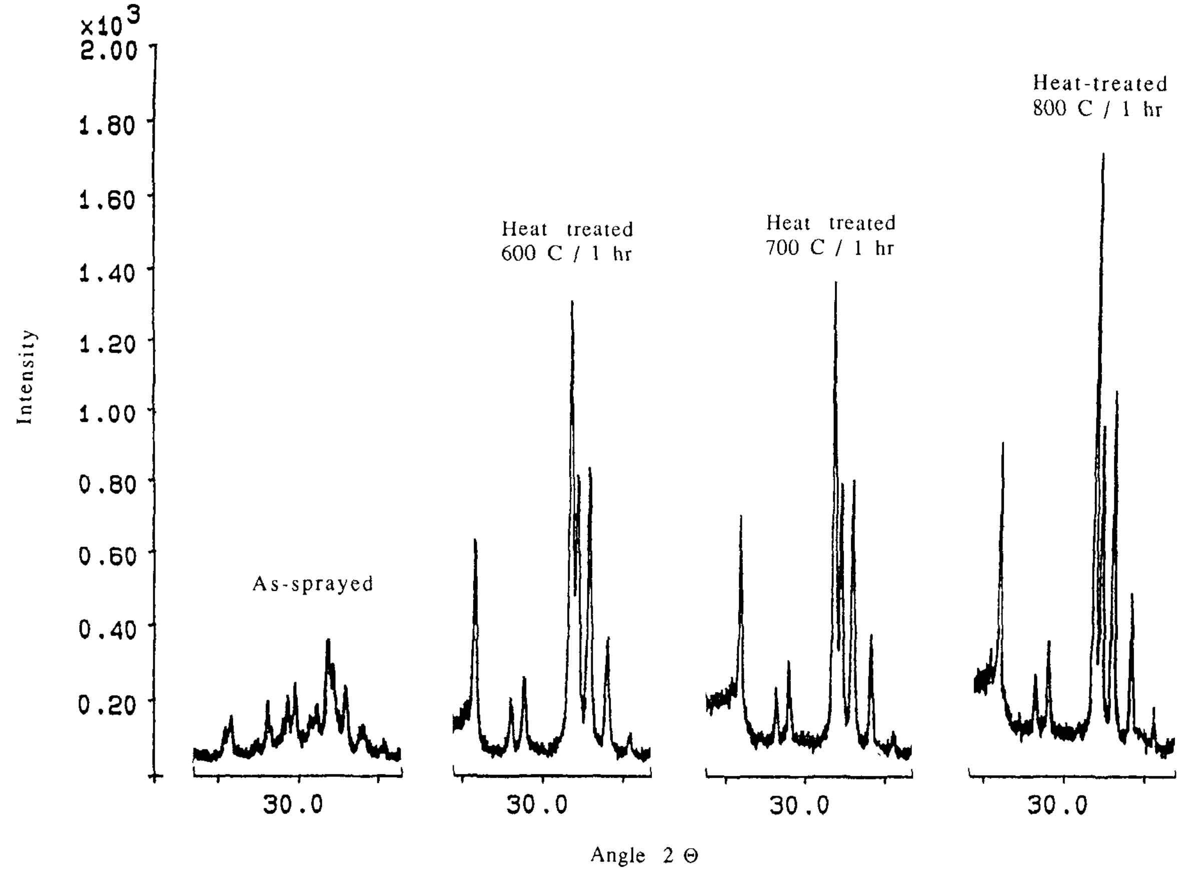

Fig. 7 XRD of heat treated plasma spheroidized 10 to 20 µm powder at 600, 700, and 800 °C. All samples were heat treated for 1 h

This variety is not uncommon, because phase changes and structural changes are characteristic of thermally sprayed coatings.[16] The formation of these phases is the result of extreme temperatures, rapid cooling, and highly reactive atmospheres that favor nonequilibrium or metastable structures. Complex multifaceted coating microstructures often result, comprising unmelted crystalline particles wedged between semi-deformed partially melted transition phases and rapidly solidified amorphous lamellar splats. An intricate network of micropores and phases is created, the extent of which is dependent on the physical nature and thermal treatment of various particles.

Results obtained from the plasma spheroidization of agglomerated powder help explain the complexity of the HA coating microstructure generated by this powder. First, particle breakdown can take place in the turbulent plasma jet, especially when weakly agglomerated powders are used. This generates streams of particles that are smaller than the starting material, which are subject to different degrees of plasma/particle interaction. Second, the physical and thermal state of the starting powder also helps determine coating phase composition and microstructure.

Large particles above a certain size, S_m, do not melt at all (Fig. 10). These particles bounce off or become lodged in the coating, generating considerable porosity. Particles between the S_m and the critical size for effective melting in the plasma jet, S_c, will be partially melted. Their outer surface will have a smooth glassy appearance, whereas their core has the structure and texture of the original starting powder. Coatings made from particles in this size range will comprise a complex array of both fused and unmelted particles. The porosity may be less than that of coatings produced from the larger size powder. Particle sizes less than S_s, the maximum spheroidization diameter, will melt completely and adopt a spherical or droplet shape prior to hitting the substrate. These droplets will form splats on the substrate with probably stronger and more coherent lamellar structures than one produced from larger particles. Particles below the size of S_a will contain the predominantly amorphous calcium phosphate phase, CaO and TCP.

The heat content and temperature of the particles will also affect the crystallinity and phases formed. At high temperatures, high-temperature phases form, which are retained during rapid cooling. Amorphous, glassy structures are also likely to form from the solidification of completely molten particles if the thermal conditions during solidification do not favor nucleation and growth of the low-temperature phases. With very small parti-

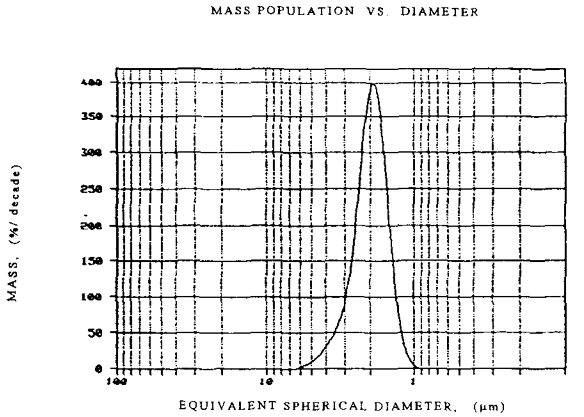

Fig. 8 Particle size distribution of fine precipitates of as-prepared HA powders

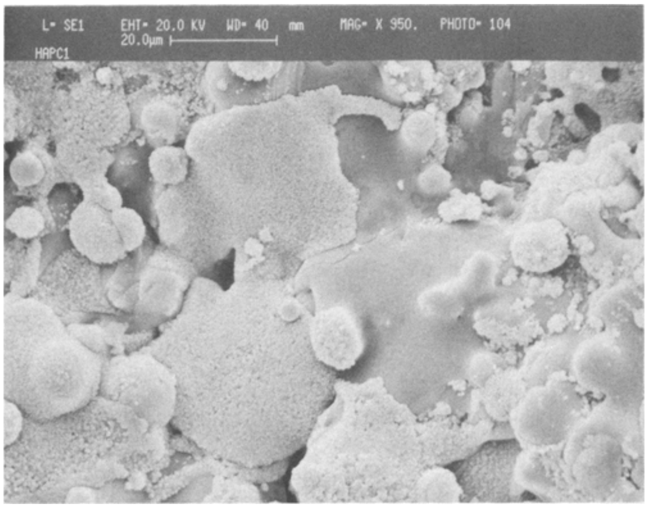

Fig. 9 Surface structure of plasma-sprayed HA coating made from calcined 56 to 75 μm powder

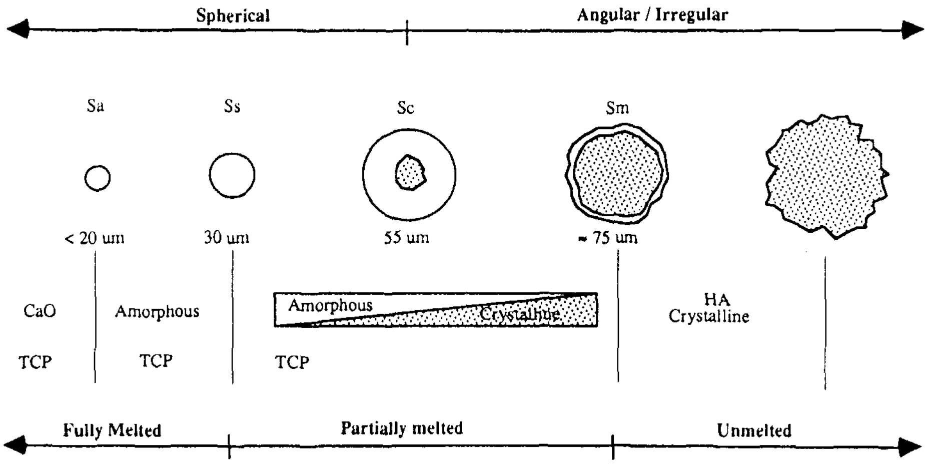

Fig. 10 Schematic of particle size and shape of HA materials during thermal spray processing

cles, overheating and vaporization can lead to dissociation and decomposition of the HA to form other compounds like CaO.

The XRD results and polarizing optical microscopy investigation show that the percentage of amorphous structure increases with decreasing particle size. The presence of TCP suggests phase transition at high temperatures. CaO is also observed for spheroidized particles less than 20 μm (10 to 20 μm).

Considering the sensitive nature of the biological environment, such a complex microstructure comprising numerous phases and structures as a result of physico-chemical changes during spraying is certain to induce a range of significant tissue responses significant to coating performance.

The solubilities of HA, TCP, and amorphous HA in the body fluids are known to be different.[17] Crystalline HA is considered nonresorbable, whereas TCP is resorbable and amorphous calcium phosphate highly resorbable. This suggests that the formation of resorbable TCP and amorphous calcium phosphate instead of nonresorbable crystalline HA will greatly alter biological response. Thus, the intended function of a thin protective bioactive coating can become severely impaired if amorphous calcium phosphate is formed instead of crystalline HA because the amorphous compound resorbs more quickly than the bone tissue grows in, exposing the underlying substrate to environmental attack. The physiological effects of CaO are not yet clear at this stage. On the other hand, a truly crystalline HA coating that is formed primarily from unmelted particles will probably have poor structural integrity and become prone to failure by detachment or rapid weakening during service.

The starting powder must have the correct size, structure, and morphology to avoid producing a heterogeneous coating. Each particle size range will generate a specific phase and coating structure. To produce a uniform coating, the powder must be stable and strong enough to prevent breaking down in the plasma and have good flow characteristics through the feed system for even and uniform deposition.

Obtaining a free-flowing, nonstatic, and stable HA powder suitable for thermal spraying has been difficult. The use of agglomerated particles produced via the wet method leads to poor coating quality because of particle breakdown. Such particles require further processing by spheroidization or PMRS to achieve the necessary particle cohesion and integrity.

A better understanding of the correlation between powder characteristics and coating microstructure is required to optimize spray parameters to achieve the desired properties, especially in biomedical applications, where performance is more sensitive to microstructure.

5. Conclusion

Thermal spraying can induce changes in the HA starting material that produce a coating with properties that are not suitable for biomedical application. The dimensional and structural nature of the powder governs the phase composition and structure of the coating. Biological response and coating performance are highly sensitive to phase composition and coating microstructure. Although crystalline HA coatings are desi[illegible]d, they do not always have good structural integrity. On the other hand, dense coatings formed from properly melted splats are highly amorphous and resorbable, unless appropriate post-heat treatments can be applied to restore their original crystalline form.

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