Production of Spherical Apatite Powders—The First Step for Optimized Thermal-Sprayed Apatite Coatings

E. Lugscheider, M. Knepper, and K.A. Gross

Regardless of the thermal spraying system, a coating can only be as good as the quality of the input powders. Powder quality in turn is dependent on the manufacturing process and conditions. Thus, it is possible to alter characteristics such as morphology, porosity, phase composition, and the mechanical strength of the individual particles. This article looks at powder agglomerations using the spray drying technique. Two different spray drying configurations were used to produce spherical apatite powders. Apatite powders could be produced with variable densities. Rotary-atomized powders possessed internal porosity as well as open porosity. More applicable for thermal spraying are the nozzle-atomized powders, which are more dense. The particle size range produced is dependent on the many parameters in the spray drying process. Hydroxyapatite is more sensitive than fluorapatite to alterations in process conditions. The powders produced were clean, free of other phases, and possessed good flowability for thermal spraying purposes.

1. Introduction

LIKE all coating processes, thermal spraying has to be regarded as a system consisting of the substrate, coating material, and coating process (Fig. 1). All components of the system and their interactions have to be optimized to obtain suitable coatings.[1]

The production of suitable apatite powders for thermal spray applications is an important step in producing bioceramic coatings with the desired characteristics. Among the most important characteristics of the spray powder are particle size, particle size distribution, and particle morphology. These determine the flow characteristics in the powder-feeding systems and the melting behavior in the plasma jet.[2] Powder production is a preliminary stage to thermal spraying in that it will determine the quality range of the coating. Coating morphology, phase composition, crystallinity, and porosity are dependent on particle characteristics, which in turn influence the behavior of a coating. Much work has been performed on the production of calcium phosphate coatings,[3-6] but little attention has been paid to the powder characteristics.

The two apatites occurring naturally within the body, fluorapatite in teeth and hydroxyapatite in bones, exhibit different thermal behavior. Synthetically produced hydroxyapatite has shown a very rich thermal chemistry,[7] but fluorapatite is relatively stable in comparison.[8] The electrostatic forces holding the groups together in fluorapatite are stronger,[9] and this could partially explain the increased stability. For hydroxyapatite in particular, it is desirable to produce particles with a spherical geometry. Spherical powders of a given size distribution are important, because they produce excellent heat transfer characteristics,[10] and consistent melting behavior, which increases deposition efficiency[11] and decreases coating porosity.[12] A uniform surface area ensures consistent melting, but the melting characteristics become erratic when the surface area, particle dimension, and mass for similarly sized powders vary. If little control is exercised over the powder specifications, then a coating with undesired phases could form with the presence of partially molten particles. The optimum particle shape from the viewpoint of flow characteristics is spherical, because the best aerodynamic performance is thus achieved.

The availability of techniques for the production of ceramic powders is more limited than with metal powders. This is due to the high melting point or possible phase transitions in ceramics upon heating. Under equilibrium conditions, fluorapatite melts at 1600 °C,[13] but hydroxyapatite transforms to tricalcium and tetracalcium phosphate at a temperature that is dependent on the partial water pressure (Fig. 2).[14]

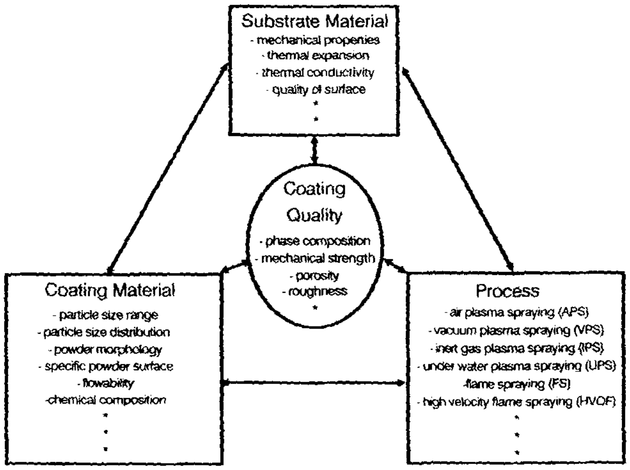

Figure 1 Plasma spraying system.

Key Words: apatite materials, biomaterial powders, particle morphology, powder processing, spray drying

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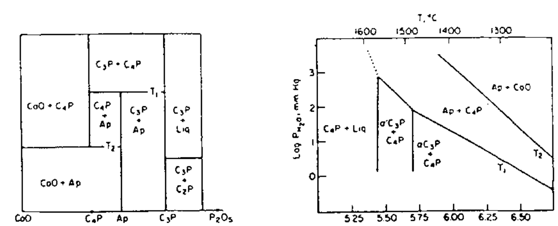
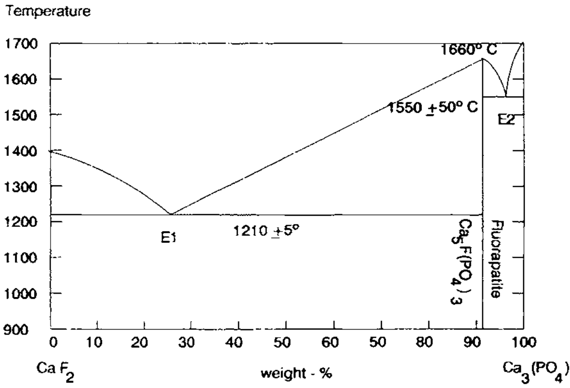


phase diagram of CaO/P_2O_5-mixture (Ap=hydroxyapatite)

phase diagram of CaO/P_2O_5-mixture showing the influence of water pressure

(a)



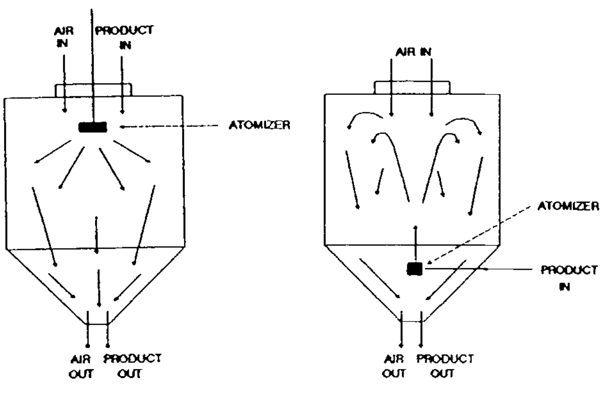
phase diagram of calcium-fluoride / calcium-phosphate

(b)

Figure 2 Phase diagrams of (**a**) hydroxyapatite (from Ref 14) and (**b**) fluorapatite (from Ref 13).

This transformation temperature can be as low as 1300 °C. High sintering temperatures and a further comminution stage for the production of apatites is not economical. Other possibilities include sol-gel and agglomeration. Sol-gel is only in the development stage[15] and has shown promise in producing very pure powders with a high bulk density and spherical morphology. Drawbacks with this technique include expensive raw materials and long production times. The production of spherical powders is most cost-effective via the route of agglomeration. Agglomeration can be performed in the synthesis stage, yielding a solid mass that undergoes mechanical attrition, or at a later stage. If the former route is chosen, then the material properties can be adjusted to yield rounded particles.[16] Other agglomeration techniques include pelletizing and spray drying. Spray drying is a preferred technique to produce spherical powders.

The most common method of producing spherical powders is the spray drying technique. This process is comparable to thermal spraying in the sense that there is an interdependence of many parameters, making it more of an art than a science. Spray drying has found wide application in the food and pharmaceutical manufacture right through to the high-tonnage outputs within such heavy chemical fields as mineral ores and clays.[17] Because ceramic powders are available in fine particle sizes, the agglomeration method via spray drying is very appropriate. The losses in this process are comparable to other powder production processes.



(a) (b)

Figure 3 Product/air flow. (**a**) Co-current flow dryer and (**b**) mixed flow dryer.

Plasma spheroidization is another processing technique that is used at the modification stage of angular or rounded particles. This offers the possibility of using a technique that produces nonspherical particles that can later be modified to a spherical morphology. Thermal spraying conditions must be chosen carefully to produce spherical, pure hydroxyapatite.[16] Despite the high quality of spheroidized powders produced by this technique, it is more time-consuming and not as cost-effective as spray drying. Plasma spheroidization can also be applied to different powder compositions. One possible use is the optimization of zirconia powders by spheroidization for thermal barrier coatings.[18]

2. Methods

2.1 *Powder Production*

The hydroxyapatite and fluorapatite source powders were provided by Friedrichsfeld, AG. The apatites were spray dried for ease of transportation. An apatite suspension was prepared by mixing one of the apatites with water and 2 wt.% binder. Too much binder can produce "bubble effects" on the surface; consequently, 2% was selected as a sufficient quantity for binding the individual components in the spray-dried particle. The binder was added in the form of a solution so that the binder particles could be dissolved before addition to the ceramic slip. This binder decomposed completely at a temperature of 450 °C. Ball milling for a period of 20 min was used to break large particles as well as to achieve a homogeneous apatite slip.

Spray drying was performed in a co-current flow dryer that could be adapted to a mixed flow dryer. In the former case, the flow of droplets within the chamber travels in the same direction as the flow of hot air, whereas in the latter case the spray droplets initially travel in the opposite direction to the hot air flow (Fig. 3). A straight vaned rotary and a centrifugal pressure nozzle atomizer were used to optimize the desired powder characteristics. The nozzle produced a solid cone spray as opposed to a

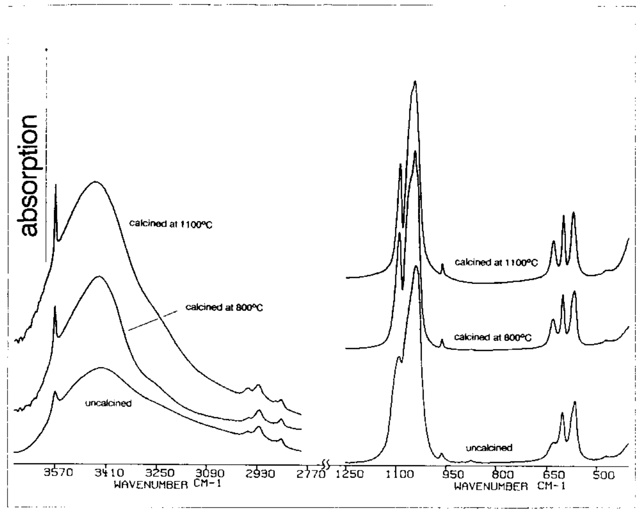


Figure 4 Infrared spectrums for as-received and spray-dried powder.

hollow cone spray. Before spray drying, the chamber environment was preheated to a sufficiently high temperature by using heated water as the feed solution.

Careful attention was given to produce an apatite slip that showed no signs of frothing. Different wheel speeds were used for rotary atomization of both the hydroxyapatite and fluorapatite slips. Wheel speeds were selected at 15000, 18000, 20000, 22000, and 25000 rpm. The effect of nozzle pressure was investigated in the nozzle atomization mode. At a pressure of 1.6 bar, the flow was not uniform. Nozzle pressures in the range of 1.6 and 2.2 bar were used. Binder content was also changed from 2 to 4%. The effect of binder concentration was only investigated with fluorapatite.

The spray-dried hydroxyapatite powder was calcined at 800 °C, and the fluorapatite was calcined at 1200 °C to remove the binder and to increase the crystallinity of the powder. Calcination was performed in an induction furnace.

2.2 *Powder Characterization*

The powders were analyzed for purity, undesired phases, crystallinity, particle size distribution, particle morphology, porosity, and flowability. Purity of the source powder and the spray-dried powder was analyzed by infrared spectroscopy. The alkali disk technique was employed using KBr as the window material. The middle infrared spectra (4000 to 400 cm^{-1}) were obtained using a Nicolet 710 SX spectrophotometer.

The phases were determined with a Phillips X-ray diffractometer. A cobalt anode was used at a voltage of 30 kV, a current of 30 mA, and the detector was operated between the angles of 25 and 65°. Changes in crystallinity were assessed by increases in the peak height. A Sedigraph 5000 was used to evaluate the particle size distribution. This technique is based on sedimentation theory and is limited to particle sizes up to 100 µm. The powder was placed in a 50% glycerol and 50% (volume percents) water medium for analysis.

Particle morphology and porosity were examined with the aid of a Joel scanning electron microscope (SEM). Powder samples were carbon coated and then observed with the accelerating voltage set to 15 kV. The powders were examined in the free-standing form as well as after polishing powders which had been embedded in setting resin.

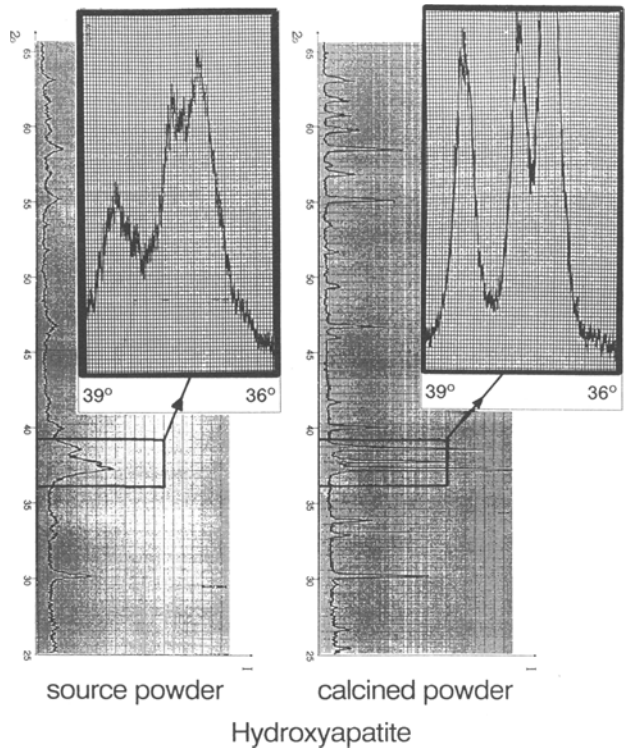


Figure 5 X-ray diffraction scans showing (**a**) the absence of other phases and (**b**) the increase in peak height after calcination.

Flowability was determined using a Hall flowmeter according to the same conditions used for testing the flowability of metal powders.[19] Spray-dried and classified powders were examined in calcined and uncalcined states.

3. Results

Hydroxyapatite powder exhibited no change in purity after spray drying. The absorptions in the infrared spectrum (Fig. 4) are typical for hydroxyapatite powders. Contamination of powders can be a problem when different powders are processed in the same spray dryer. Stringent, clean conditions must be observed for production of powders for biomedical applications, which may be used directly or further processed before implantation.

X-ray diffraction showed that no other calcium phosphate or undesired phases could be identified. The source powder exhibited a low crystallinity typical for apatites produced by the wet method. After calcination, the powder showed, what is thought to be, an increase in crystallinity as assessed from the peak height (Fig. 5).

The degree of crystallinity was not evaluated, because the increase in peak height and an accompanying decrease of the half peak height width can also be interpreted as an increase in crystal size. Calcination could increase both the crystallinity and the crystal size. X-ray diffraction by itself is not sufficient in determining this change and must be used in conjunction with transmission electron microscopy or infrared spectroscopy to understand the change more completely. Little or no transmission electron microscopy work has been published showing the increase in crystal size with calcination. Infrared spectroscopy (Fig. 4) shows that some peaks are more easily resolved after calcination. This implies that the crystal lattice is more defined and indicates an increase in crystallinity. After heat treatment, the absorptions for the phosphorus groups at about 640 and 1080 cm^{-1} are more easily distinguished.

Spray drying offers a variation in particle morphologies and porosities. The use of a rotary atomizer led to porous particles with a sphere-like morphology (Fig. 6). Pores were found in both apatites in the form of open and closed porosity. The hydroxyapatite powders exhibited small surface depressions. This behavior is typical for droplets that undergo quick evaporation. Contraction of the droplet occurs on the external surface and internally. By controlling the drying sequence, one can obtain the required porosity. Calcination of the apatites produced no change in the macrostructure of the particles.

The particle microstructure produced by the rotary atomizer can be explained with reference to the source powder and the spray dryer. Liquid droplets leaving the wheel atomizer experience rapid solidification when they make initial contact with the hot air. A solid shell is rapidly formed, and further drying leads to a small amount of contraction, which is observed as small surface impressions. Further drying occurs by diffusion through this solid shell. This is the normal drying sequence for liquids within a drying chamber. The unusual presence of the spherical particles within the pores can be explained by insufficient milling of the source powder. The bulk of the interior, still possessing a fraction of moisture, is plastic, and a void of spherical geometry is formed to minimize the surface energy of this new internal surface.

Nozzle atomization is useful in the preparation of spherical particles with a higher density (Fig. 7). The change in density from the rotary-atomized powders was not quantitatively as-

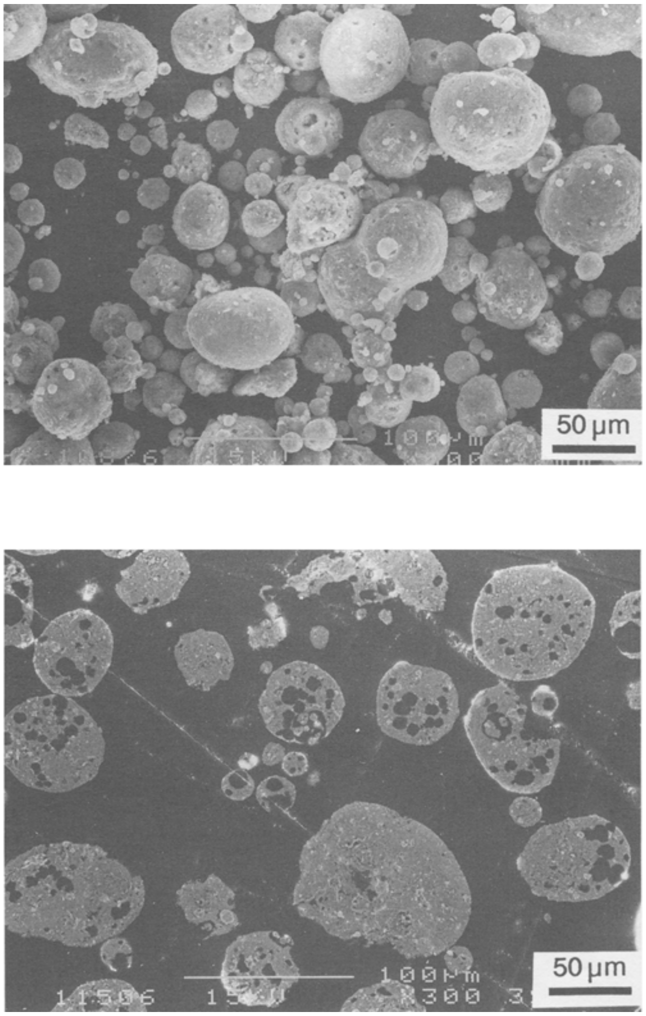


Figure 6 Morphology and porosity produced by rotary atomization (SEM).

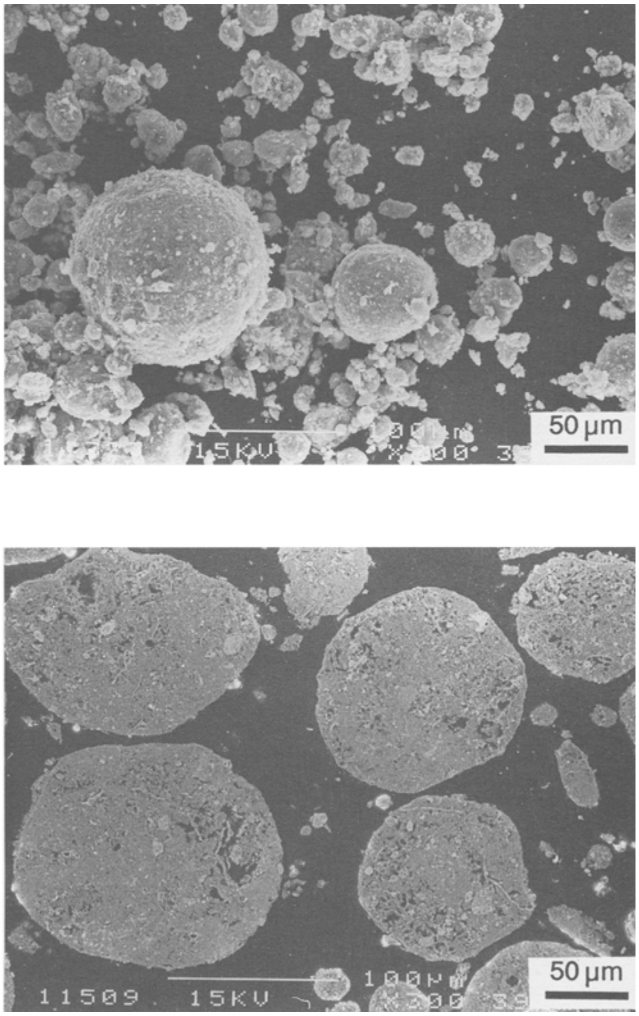


Figure 7 Morphology and porosity produced by nozzle atomization (SEM).

sessed. A denser powder was produced due to the less severe heat treatment in the spray drying operation.

During the process of nozzle atomization, the heating cycle is much longer and not as severe as in rotary atomization. The liquid is able to evaporate more slowly, leading to a more dense product. Small spherical particles are included in the bulk material of the particle with minimal connected porosity.

The particle size range exhibited a dependency on various parameters. In using rotary atomization, a feed solution with a lower viscosity was preferred in yielding particles of a larger mean size distribution (Fig. 8). The solution can leave the wheel more easily in a fluid state to form large droplets, which are then dried to form particles. Wheel speed is another determining factor, and decreasing the parameter again leads to larger particle sizes (Fig. 9). This atomization process produced powders within a fairly narrow particle size range that could be suitable for vacuum plasma spraying.

Nozzle atomization was easier to control. The mean particle size was larger, and a wide size distribution was obtained in all cases. This offers the advantage of producing powders suitable for different thermal spraying processes. Nozzle pressure had the most influence on the mean particle size. By increasing the pressure, the mean particle size was observed to decrease (Fig. 10). The air has more kinetic energy and is able to break up the droplets. By using a thicker consistency, a larger mean particle size is produced. This evaluation was carried out only with fluorapatite, which was more insensitive to changes in process parameters.

The mean particle size was smaller for fluorapatite than hydroxyapatite. A change of the OH^- group to an F^- in the crystal structure changes the surface characteristics of the apatite. By

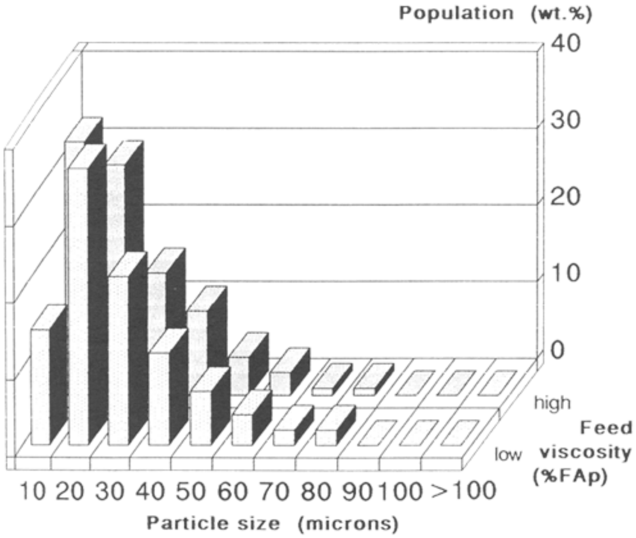


Figure 8 Particle size distribution from different feed solution viscosities.

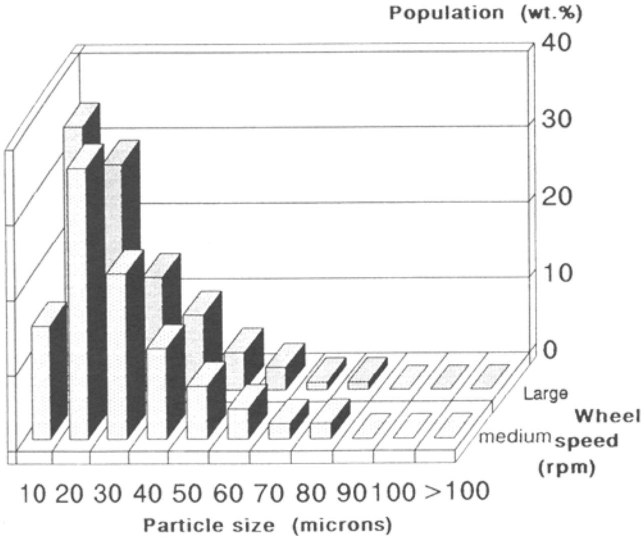


Figure 9 Effect of wheel speed on particle size distribution.

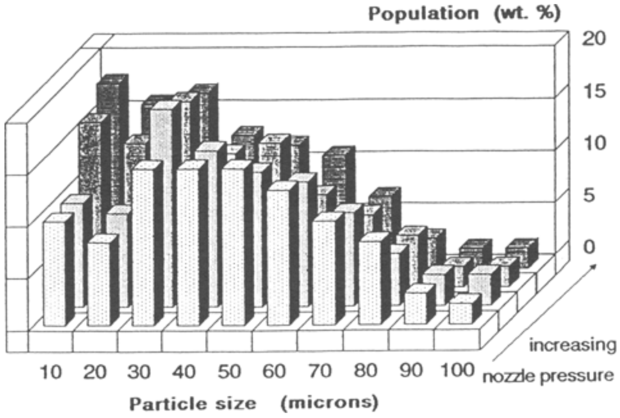


Figure 10 Effect of nozzle pressure on particle size distribution.

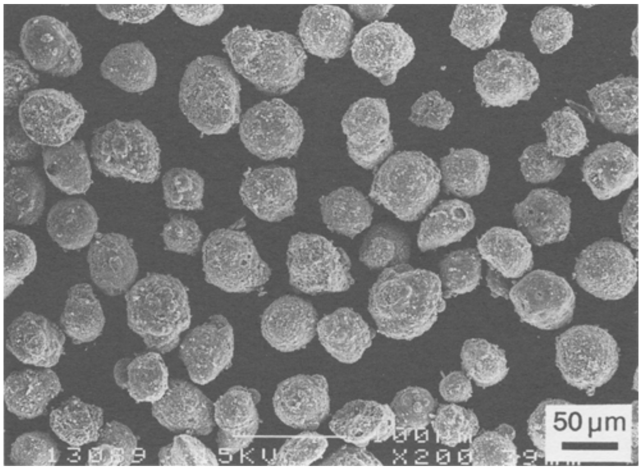
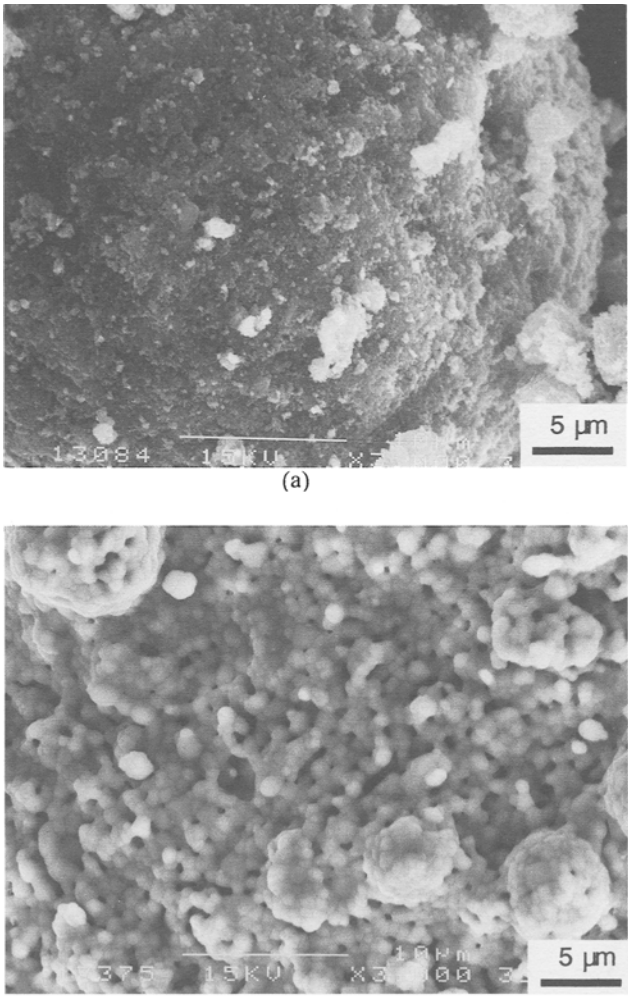


Figure 11 Powder of desired morphology and particle size distribution for thermal spraying.

adding the two apatites together in equal quantities, a powder with a level particle size distribution can be produced.

The classified powder shown in Fig. 11 is spherical in nature, and the particles are reasonably uniform in size. This is desired for thermal spraying so that one can ensure that the particles have identical trajectories and a similar thermal history within the plasma effluent. This is more important for hydroxyapatite than fluorapatite because of the ease of producing other calcium phosphates and an amorphous phase for the former material.



(a)

(b)

Figure 12 Surface of calcined (**a**) hydroxyapatite and (**b**) fluorapatite powders.

The flowability determined using the Hall flowmeter was very satisfactory for the classified powders (Table 1). Unclassified powders exhibited a pulsating flow and low flowability. This is due to the very wide particle size distribution in the powder. Powder classified to a smaller average particle size produced a lower flowability, and this is in agreement with the findings of Krasnov.[20] Pulsating was also observed in some classified powders (see Table 1).

Calcination lowered the flowability of hydroxyapatite powder. Removal of binder from the particles led to the formation of a surface with greater roughness, which decreased flowability. A rougher surface could also arise from adhesion of small fines to the surface of particles. This is seen clearly with the dense hydroxyapatite powders. Porous hydroxyapatite powders exhibiting significant initial surface roughness undergo a smaller change. Common to both dense and porous particles is the adhesion of fines to the surface by secondary bonding. Calcined fluorapatite, however, possesses a smoother surface (Fig. 12), and this leads to greater flowability. Small spheres (about 1 µm in size), larger in size than the fines observed on hydroxyapatite particles, appear to have fused together. The surface is more defined, and the porosity appears to be higher. The post-heat treatment thus plays a role in altering flowability, but must be chosen carefully to prevent other undesirable changes in the properties of the powder.

4. Conclusion

Spray drying of apatite powders for thermal spray applications produces powders with properties that are acceptable for the thermal spray process. Investigations with hydroxyapatite and fluorapatite show that it is possible to produce powders with different porosity. Rotary-atomized powders however produced internal porosity as well as open porosity. More dense powders can be produced by nozzle atomization. The operational parameters have a significant influence on the particle size range. The sieving process must be performed for both spray drying modes examined so that suitable particle size distributions can be obtained for thermal spray processing. Investigations showed that hydroxyapatite is more sensitive to operational parameters in spray drying compared to fluorapatite.

By X-ray investigations, it could also be shown that a calcination process is necessary for achieving apatite powders with high crystallinity. The increase of crystallinity could also be ob-

Table 1 Flowability of Spray-Dried Powders [g/sec]

Particle size range,	Powder type				
	Noncalcined		Calcined		
µm	Dense hydroxyapatite	Porous hydroxyapatite	Dense hydroxyapatite	Porous hydroxyapatite	Dense fluorapatite
45 to 63	0.15	...	...	...	No flow
45 to 80	0.20	0.18	0.11(a)	0.13(a)	...
63 to 80	0.22	...	...	...	0.44
80 to 125	0.27	...	0.25	0.22	0.54

(a) These powders exhibited a pulsating type of flow.

served by infrared spectroscopy. These characterizations also showed that the powders produced were clean and free of other phases and possessed good flowability for thermal spraying.

Acknowledgments

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