

Spray-drying of ceramics for plasma-spray coating

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Received 15 January 2000; received in revised form 29 March 2000; accepted 2 April 2000

Abstract

The spray-drying process of ceramics which are candidate materials for thermal barrier coatings (TBCs), i.e. 3YSZ+0, 2, 4, 6 wt.% Al₂O₃, is discussed in this paper. The two most important properties of spray-dried powders to determine the coating quality are density and particle size. Polyethyleneimine (PEI) acts as both an organic binder and a dispersant giving low viscosity in the suspension. The optimised suspension composition is: ≥ 33.6 vol.% powder + 1.8 wt.% PEI + ethanol, and operational parameters of the spray-dryer: drying temperature 175°C, feeding rate 55 cm³/min, feeding pressure 1.013×10⁴ Pa. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Plasma spraying; Spray-drying; Thermal barrier coatings; ZrO₂-Al₂O₃

1. Introduction

Spray-drying is a process by which a fluid feed material is transformed into a dry powder by spraying the feed into a hot medium. The feed materials are either water-based suspensions with air as drying gas or organic solvent-based suspensions (usually ethanol) with nitrogen as drying gas.¹ In general, there are five factors to influence the characteristics of spray-dried powders: type of atomiser, suspension composition, feeding rate, drying temperature and atomising pressure.^{2–4} The spray-drying theory for ceramics has been discussed by Lukaszewicz⁵ and Masters.⁶

The spray process is a result of many interwoven complex mechanisms and no comprehensive mathematical treatment of atomisation has been developed.⁷ For external-mixing nozzles (as the type used in this work), one generally applied empirical equation to predict the mean drop size is as follows:⁷

$$SMD = C \left(\frac{\rho_L^{0.25} \mu_L^{0.06} \sigma^{0.375}}{\rho_A^{0.375}} \right) \left(\frac{\dot{m}_L}{\dot{m}_L U_L + \dot{m}_A U_A} \right)^{0.55} \quad (1)$$

SMD is Sauter median diameter, *C* a constant whose value depends on nozzle design; ρ , μ , σ , *U* and \dot{m} are density, viscosity, surface tension, velocity and flow rate of the liquid (L) or air (A), respectively.

The compaction of spray-dried powders has received considerable attention in the literature.^{3,8–11} Due to its high flowability and hence the achieved high green density, the spray-dried powder can provide sintered bodies with high densities and highly precise dimensions. The particle size, the size distribution and the particle strength, which determines the behaviour during cold compaction, are the most important parameters for a spray-dried powder with high sinterability.

A new application of spray-dried powders in TBCs has been developed.^{12,13} Spray-dried powders offer an advantage in the application of TBCs where a high porosity (10–20%) is necessary. On the other hand, particles of the spray-dried powders are usually spherical and free flowing, the powder can be easily fed by the plasma-spraying gun. As reported by Wigren,¹⁴ the coating whose starting powders were prepared by spray-drying/sintering had longer thermal shock lives than those coatings whose powders were prepared by precipitation, sintering/crushing and hollow-spherical-powder (HOSP). However, not all the spray-dried powders are suitable for plasma-spray coating. Both the particle size and particle density are critical to the coating

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quality. The powder should be dense enough and have a proper size distribution. If the powder is fine and porous, it can not be fed into the centre of the plasma flame and will float on the flame surface or be evaporated by superheating before spitting on the substrate, resulting in a poor deposition efficiency and poor coating-bond strength. In our experiment, we find that the spray-dried powder with bulk density $> 1.7 \times 10^3 \text{ kg/m}^3$ and mean particle size $> 20 \mu\text{m}$ can be directly used for plasma-spray coating even without further densification.

In this paper, we will discuss the spray-drying process of ceramics and the method to prepare powders with high density and large particle size. The property of TBCs will be reported separately.

2. Experimental

The spray-dryer was a Mobile MinorTM2000' Ex Model H (Niro A/S) with N_2 as the drying medium, a pneumatic nozzle (external mixing), and a drying capacity of 1–5 kg water/h. Fine powder and coarse powder were collected from the cyclone and the drying chamber, respectively. The powder collected from the drying chamber (named as “chamber powder” for the reason of simplicity) is much more flowable and has much larger particle size than the powder collected from the cyclone (named as “cyclone powder”). Only the chamber powder was suitable for plasma-spray coating. Suspensions for spray-drying were made by mixing ceramic powder with ethanol and then ball-milling for longer than 24 h. In order to reduce the viscosity of suspension, PEI was added ($[\text{CH}_2\text{CH}_2\text{NH}]_x$, m.w 1×10^4 , Polyscience). It is stable below 300°C as proved by thermogravimetric analysis. The amount of PEI was based on the weight of dry powder. The suspension viscosity was measured with a viscometer (Haake TP 500, Germany) at a shear rate of 150 s^{-1} . The cyclone powder can be reused by mixing with ethanol, sonicating in an ultrasonic bath to form suspension and repeating the drying procedure. Particles of the spray-dried powder can be easily crushed by an ultrasonic wave. bulk density of the powder was determined by measuring the weight of a volume of powder with a graduate cylinder which was gently tapped until a constant volume was obtained (JEL, Stampfvolumeter Stav 2003, Germany). Apparent density of the powder was measured by a fluid-immersion method, and the volume percentage of powder in suspension is based on this density. Particle size of the chamber powder was determined by means of laser-scattering. Chemicals used in this work: 3YSZ (3 mol% yttria stabilised zirconia, Tosoh; apparent density $5.28 \times 10^3 \text{ kg/m}^3$), Al_2O_3 (Martoxid, CS-400/M, 99.8%, apparent density $3.43 \times 10^3 \text{ kg/m}^3$, $\alpha\text{-Al}_2\text{O}_3 \geq 90\%$). The morphology of spray-dried powder was observed by SEM, scanning electron microscope (JEOL, JSM-T300, Japan).

3. Results and discussion

3.1. Process of spray-drying

Although spray-drying is a complex process, we propose a simple mechanism to describe the spray-drying process of ceramics with four steps as illustrated in Fig. 1: (1) droplet formation, (2) evaporation and ballooning, (3) explosion and (4) particle formation.

The drying gas is introduced through the ceiling to the drying chamber. When the suspension is pumped into the drying chamber, it is separated into small droplets immediately by the compressed feeding gas. Afterwards, the droplet shrinks because of the fast evaporation of solvent.

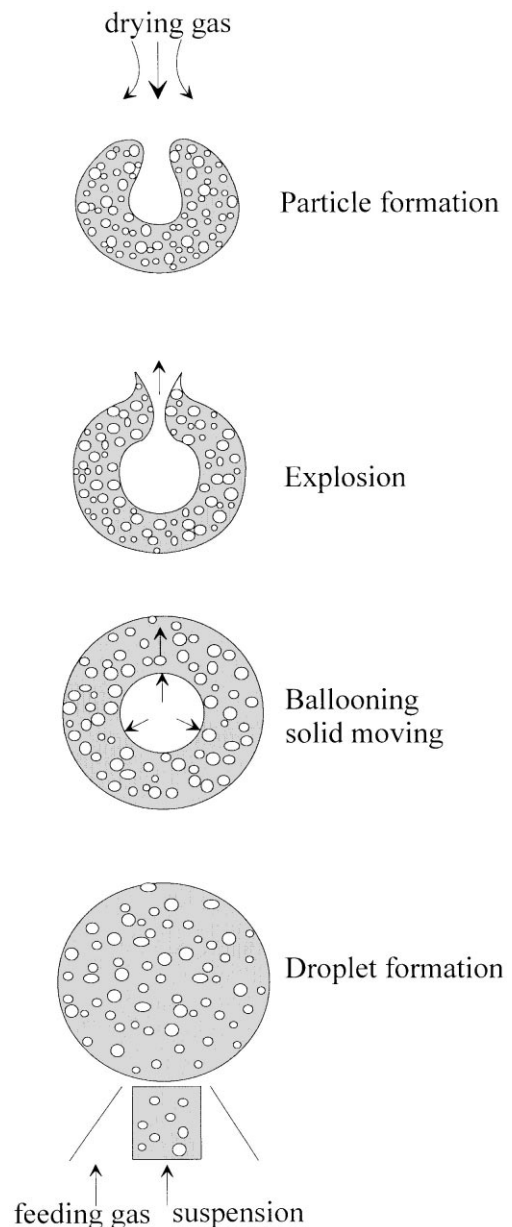


Fig. 1. Spray-drying process of ceramics.

During the process of liquid moving from the inside to the outside of the droplet, the solid particles are also carried along. Inside the droplet, a void is produced when the evaporation rate inside the droplet is higher than the diffusion rate through the droplet surface. When the pressure inside the droplet reaches some limit, explosion is not avoidable. In the fourth step, the particle is plasticized by the loss of solvent and the addition of organic binder. The plasticized droplet shrinks continuously due to the effect of surface tension until it is totally dried. The particle size should be mainly determined by the third step at which most of the solvent has been lost and a soft shell is formed. We assume the surface tension of this soft droplet to be σ_d and the temperature at the centre of the droplet to be T .

The pressure difference between the inside and outside of the droplet can be calculated with the following expression:

$$\Delta P = P_{\text{in}} - P_A = \frac{2\sigma_d}{r_1} \quad (2)$$

P_A is the ambient pressure inside the drying chamber, r_1 the radius of the hollow centre of the droplet and P_{in} the pressure inside the droplet which is the limit when the droplet begins to explode.

P_{in} can be calculated with the following equation:

$$PV = nRT = P_{\text{in}} \left(\frac{4\pi}{3} r_1^3 \right) = \left(\frac{4\pi}{3} r_0^3 \alpha C_1 \rho_l / M \right) RT \quad (3)$$

r_0 is the original radius of the suspension droplet when it is newly formed, C_1 the solvent content (volume percentage) in the droplet, α is the percentage of solvent which exists inside the droplet in the state of gas before the droplet explodes, ρ_l and M the density and molecular weight of the solvent, respectively.

The relationship of r_0 and r_1 can be expressed as:

$$r_0^3 = \frac{2\sigma_d M}{\alpha C_1 \rho_l RT} \left(r_1^2 + \frac{P_A}{2\sigma_d} r_1^3 \right) \quad (4)$$

In the spray-dried particle, the powder volume can be calculated with:

$$\Delta V = \frac{4}{3} \pi (r_2^3 - r_1^3) \varphi \quad (5)$$

φ is the volume fraction of the powder, i.e. packing factor and r_2 the outer radius of the droplet. For crystalline materials, the packing factor is between 74% (the closest rhombohedral packing) and 52% (the most open cubic packing). In the suspension droplet, the powder volume is:

$$\Delta V = \frac{4}{3} \pi r_0^3 (1 - C_1) \quad (6)$$

Fig. 2 shows the cross-section microstructure of a spray-dried powder SPL17 (3YSZ + 6 wt.% Al_2O_3). This powder has a mean particle size 39.8 μm . In the picture, $r_2 \approx 20 \mu\text{m}$, $r_1 \approx 10 \mu\text{m}$, $\frac{r_1}{r_2} \approx 0.5$. The powder content in the suspension was 15.0 vol.%. Assuming φ is between 0.3 and 0.6, then r_0 ranges from 24 to 30 μm , larger than r_2 , proving that the droplet shrinks during the drying process. Surface tensions of organic liquids rarely reach 0.1 N m^{-1} especially above 100°C.¹⁵ For the mixture of ceramic powder, PEI and ethanol of this case, it is reasonable to assume $\sigma_d < 0.1 \text{ N m}^{-1}$. As calculated with equation (4), the parameter α has a value on the level $10^{-9} \sim 10^{-8}$, indicating that the droplet loses solvent mostly by the evaporation through the surface. As observed by Duffie and Marshall,² for balloon-forming materials such as potassium nitrate the spray-dried particle had a size about 2000 μm but the wall-thickness was only 5–20 μm , so the ratio $\frac{r_1}{r_2} \approx 0.99$.

3.2. Factors influencing the properties of spray-dried powders

3.2.1. Operational parameters of the spray-dryer

The suspension for spray drying was: 15.0 vol.% 3YSZ + 1.5 wt.% PEI + ethanol. The relationship between the particle size/bulk density and the drying condition is summarised in Table 1.

The influence of temperature on the particle-size can be observed by comparing experiments 3/4 and 5/6; other effects: feeding rate by 1/3 and 2/4, feeding pressure by 1/5, 2/6.

It is obvious that among these three effects, feeding-rate is the most effective one. The effectiveness order is: feeding-rate > feeding pressure > drying temperature.

The effect of drying temperature is multifold. First, the higher is the drying temperature the larger is the droplet ballooning [r_1 in Eq. (4) increases] and the larger

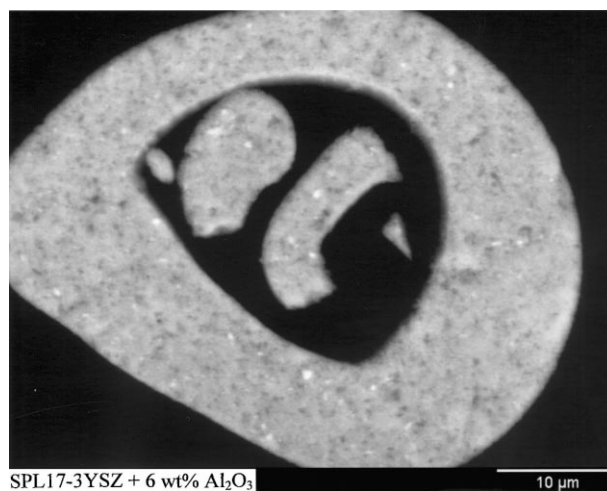


Fig. 2. Scanning electron micrograph of the cross-section structure of spray-dried powder.

Table 1
Influence of operational parameters of the spray-dryer on the properties of dried powders

Sample	Temperature (°C)	Feeding rate (cm ³ /min)	Feeding pressure ($\times 1.013 \times 10^5$ Pa)	ϕ_{50}^a (μm)	d_b^a ($\times 10^3$ kg/m ³)
SPL1	160	60	0.4	16.5	1.50
SPL2	145	55	0.4	15.3	1.49
SPL3	160	25	0.4	10.8	1.42
SPL4	145	25	0.4	10.7	1.52
SPL5	175	55	0.1	20.5	1.60
SPL6	145	25	0.1	18.8	1.64

^a ϕ_{50} and d_b are the mean particle size and bulk density of the dried powder, respectively.

is the particle size; second, the higher is the temperature the lower is the surface tension of the droplet, resulting in an increase of particle size; third, the warm-up period of drying is shortened by fast heating and thus crust formation starts earlier in the drying process resulting in a decrease in particle size.

Because the bulk density of powder is directly proportional to the apparent density of particles, the mass of particle should also be directly proportional to the bulk density. SPL5 has the highest $\phi_{50}^3 d_b$ value and hence the optimised operational parameters of the spray-dryer can be formed: drying temperature 175°C, feeding rate 55 cm³/min, feeding pressure 1.013×10^4 Pa.

3.2.2. Suspension preparation

Suspension preparation is believed to be more important than the operational parameters of the spray-dryer to influence the characteristics of the dried powder. The influence of suspension preparation on the powder characteristics is shown in Table 2. The operational parameters of the spray-dryer were: drying temperature 175°C, feeding rate 55 cm³/min, feeding pressure 1.013×10^4 Pa.

The powder content in the suspension has a strong influence on both the density and particle size of the dried powder (SPL7–9, 13). The increase of powder content results in an increase of suspension viscosity and also gives rise to the formation of dense powder. The influence of powder content on the particle size includes two counter effects. As discussed above, the particle size r_2 includes two parts, i.e. the hollow centre size r_1 and the wall-thickness. The lower is the solid content in the suspension, the larger is the ballooning (r_1 larger) but the thinner is the wall thickness. The final result depends on these two effects. For low solid-content suspension (SPL7–9, < 35 vol.%), the particle size decreases and the density increases with the increase of solid content; for high solid-content suspension (SPL13, > 50 vol.%), both the particle size and density increase with the increase of solid content. 52.2 vol.% is the maximum solid content in the suspension.

The addition of PEI does not change the viscosity on a large scale (SPL7, 10–12). 1.8 wt.% is the optimised

PEI content whose dried powder has the highest density and largest particle size. The specific area of PEI molecules is estimated to be less than 900 m²/g by taking into account the bond length of C–H, C–C and C–N. After being ball-milled, the mean size of the powder in suspension is about 0.3 μm . In order to make individual particles combined with each other strongly, the individual particle should be covered at least by one layer of PEI molecules, i.e. 0.25 g PEI/100 g 3YSZ. 1.8 wt.% is about 7 times this theoretical value. Too much binder leads to a loosely combined structure.

SPL10 has a comparatively high bulk density 1.75×10^3 kg/m³ and large mean size 22 μm , this powder is suitable for plasma-spray coating.

Water has a much higher surface tension (72.8×10^{-3} N/m, 25°C) than ethanol (22.0×10^{-3} N/m, 25°C). Water-based suspension will be expected to produce particles with a mean size 57% larger than that of the ethanol-based suspension if other experimental conditions are kept constant as calculated with Eq. (1). However, water has a much higher heat capacity than ethanol. The feeding rate 50 cm³/min of ethanol evaporation is equal to 15 cm³/min of water evaporation. The low feeding rate of the water-based suspension will result in a large decrease of particle size according to the conclusion of section A. We tried the water-based suspension with feeding rate 15 cm³/min, and produced a powder with mean particle size < 10 μm .

From the above experimental results, we conclude the optimised suspension composition as: ≥ 33.6 vol.% powder + 1.8 wt.% PEI + ethanol.

3.2.3. Organic binder

The organic binder keeps the solid particles combined with each other. In ceramic processing, cellulose derivatives and PVA (polyvinyl alcohol) are most popular binders.^{11,16,17} The cellulose binder probably gives the most outstanding increase in dry strengths for all ceramic products.¹⁷ In this work, we tried two cellulose derivatives, i.e. ethylcellulose which is soluble in organic solvent and hydroxyethylcellulose which is water-soluble. Fig. 3 shows the effect of ethylcellulose addition on the viscosity of the suspension and the bulk density of

Table 2
Influence of suspension preparation on the properties of dried powders

Sample	Powder (vol.%)	PEI (wt.%)	Viscosity (Pa s)	ϕ_{50} (μm)	d_b ($\times 10^3 \text{ kg/m}^3$)
SPL7	33.6	1.5	0.23	16.3	1.68
SPL8	30.7	1.5	0.22	16.3	1.63
SPL9	28.3	1.5	0.18	18.7	1.39
SPL10	33.6	1.8	0.23	21.3	1.75
SPL11	33.6	2.1	0.25	20.8	1.61
SPL12	33.6	2.4	0.24	21.4	1.64
SPL13	52.2	1.8	0.28	42.6	2.55

the dried powder. The addition of cellulose increases the viscosity on a large scale but unexpectedly decreases the powder density sharply. All those spray-dried powders have densities lower than $1.7 \times 10^3 \text{ kg/m}^3$ and mean particle size smaller than $7.5 \mu\text{m}$. As indicated by Wild¹⁸ and Knapp,¹⁹ one of the principal shortcomings of cellulose binders is that they swell up and crack during rapid drying. It is also observed that the addition of PVA binder makes the powder density decrease.^{11,20} There is also a decrease of powder density with the addition of PEI when its content is too high (Table 2, SPL10–12), but this effect is not as serious as that of cellulose. For the application of spray-dried powders in plasma-spray coating, cellulose is not a good binder.

3.2.4. Composite materials

Suspension compositions are: 15.0 vol.% powder + 1.5 wt.% PEI + ethanol; powder compositions are: SPL14 (3YSZ), SPL15 (3YSZ + 2 wt.% Al_2O_3), SPL16

(3YSZ + 4 wt.% Al_2O_3), SPL17 (3YSZ + 6 wt.% Al_2O_3), SPL18 (3YSZ + 6 wt.% Al_2O_3 , starting powder calcined at 1200°C for 10 h before drying). The addition of Al_2O_3 was based on the weight of 3YSZ.

Operational parameters of the spray-dryer: temperature $160 \pm 5^\circ\text{C}$, feeding rate $50 \text{ cm}^3/\text{min}$, feeding pressure $1.013 \times 10^4 \text{ Pa}$.

Results are shown in Fig. 4. The addition of Al_2O_3 results in a sharp increase of particle size and a decrease of bulk density. This phenomenon may be explained by the following two ways. The first, this as-received alumina powder has a high content of transition aluminas ($< 10\%$). It is well-known that Al_2O_3 especially $\gamma\text{-Al}_2\text{O}_3$ can be hydrated in aqueous solutions with the formation of aluminium hydroxide which is a gel-like material. The solubility of alumina is enhanced in the pH range $\text{pH} < 5$ or $\text{pH} > 9.5$.²¹ For alumina powders composed of 100% $\alpha\text{-Al}_2\text{O}_3$, the hydration is of little significance, since they normally have surface areas below $20 \text{ m}^2/\text{g}$, but the transition phases such as $\gamma\text{-Al}_2\text{O}_3$ normally have

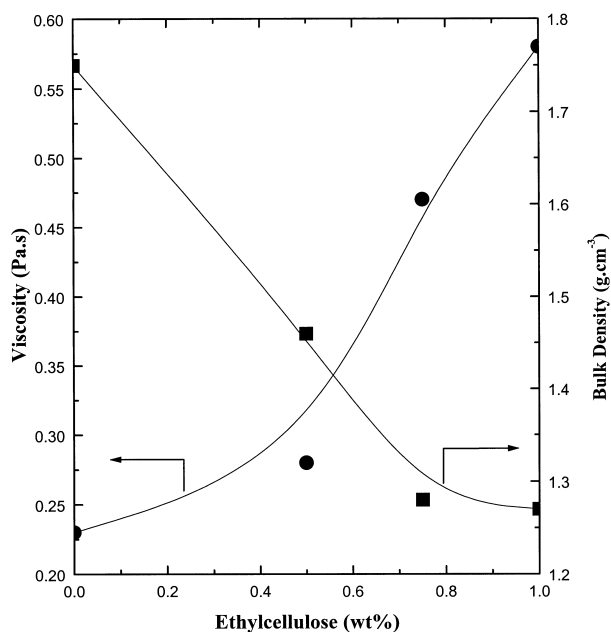


Fig. 3. Influence of ethylcellulose addition on the viscosity of suspensions and the bulk density of spray-dried powders. Suspension 33.6 vol.% 3YSZ + 1.8 wt.% PEI + ethylcellulose.

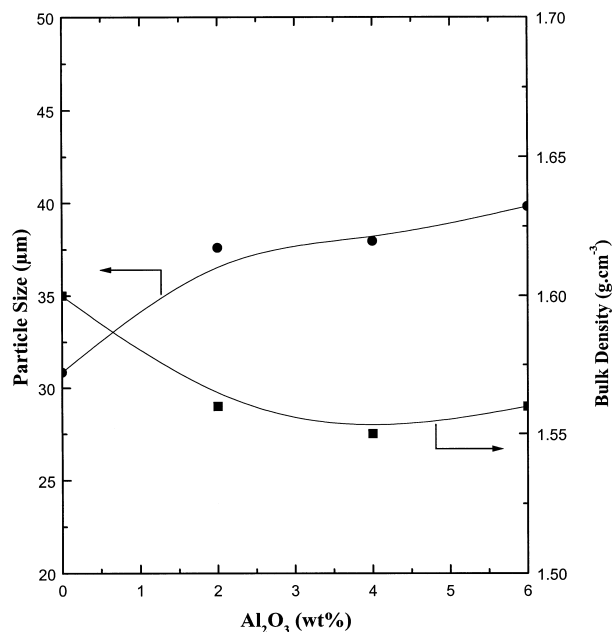


Fig. 4. Influence of Al_2O_3 -addition on the particle size and bulk density of spray-dried powders.

surface areas above $100 \text{ m}^2/\text{g}$, especially the attrition during milling continuously removes the hydration product and the extent of the reaction during long time milling is quite significant.²² Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ is a high polar solvent with a functional group $-\text{OH}$. The dispersant PEI also has a high polar functional group $-\text{NH}$. The pH value of PEI solution in ethanol (the same PEI content as in the suspension for spray-drying) is above 11. Although the solubility of alumina in ethanol is certainly not as high as in water, this effect can not be omitted. During drying, an aluminium oxide gel precipitates which is a balloon-forming material and therefore the particle size of spray-dried powder will be increased. If alumina powder is calcined above 1000°C , all transition phases in the powder will transform into $\alpha\text{-Al}_2\text{O}_3$, this is one reason for the decrease of particle size of spray-dried powder when the alumina powder was calcined (Fig. 5c of the next section). This phenomenon is reproducible even for the spray-drying of other composite materials such as $\text{CeO}_2 + \text{Al}_2\text{O}_3$ as proved in our experiment.

The second is the density difference between Al_2O_3 and ZrO_2 powders. The Al_2O_3 powder is porous with a low apparent density $3.43 \times 10^3 \text{ kg/m}^3$, while 3YSZ has a higher density $5.28 \times 10^3 \text{ kg/m}^3$. During the drying process, solid particles are carried along when the liquid flows to the droplet surface and evaporates. It is reasonable to assume that porous and low-mass particles are easy to be carried along by the moving liquid, resulting in an increase of particle size.

3.3. Structure of the spray-dried powder

For comparison, Fig. 5 shows microphotographs of some spray-dried powders. SPL10 (3YSZ) (Fig. 5a) has a smooth surface explaining why this powder has a good flowability. The particle is an agglomeration of small particles which are combined with each other tightly by organic binder.

Fig. 5b shows the microstructure of SPL17 (3YSZ + 6 wt.% Al_2O_3). Particles of this powder have much larger

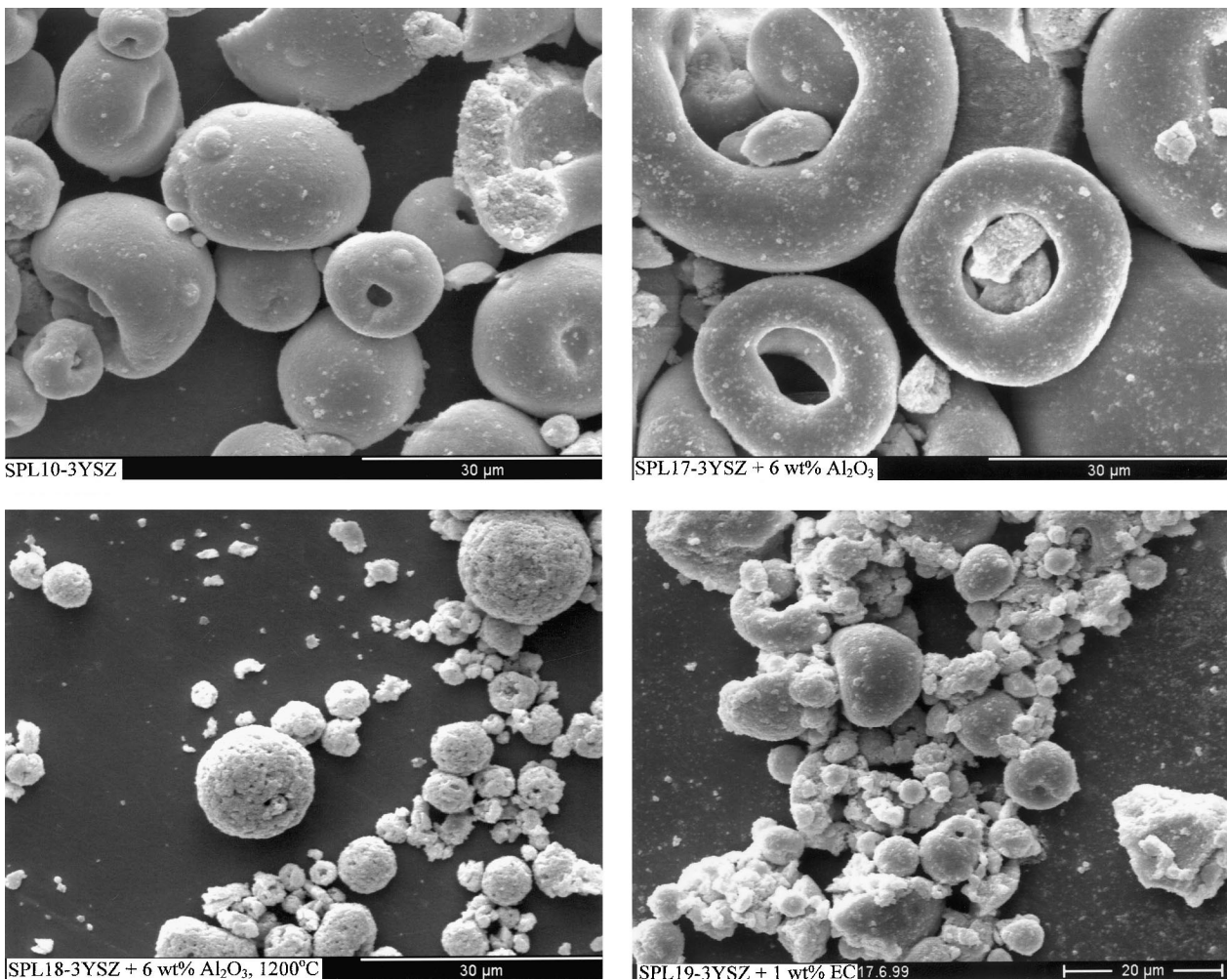


Fig. 5. Scanning electron micrographs of spray-dried powders: (a) SPL10 (3YSZ); (b) SPL17 (3YSZ + 6 wt.% Al_2O_3); (c) SPL18 (3YSZ + 6 wt.% Al_2O_3 , starting powder calcined 1200°C , 10 h); (d) SPL19 (3YSZ + 1.8 wt.% PEI + 1 wt.% ethylcellulose).

hollow centres than those of SPL10 (3YSZ) with a low bulk density (1.56 g/cm^3) and large mean size ($39.8 \mu\text{m}$). This powder can hardly be used for plasma-spraying because of its low density although its particle size is large.

Fig. 5c is the powder of SPL18 (3YSZ + 6 wt.% Al_2O_3) whose starting powder was densified by calcination at 1200°C for 10 h before drying. The particles are much smaller and more spherical than those of other powders. After milling, this densified starting powder still has a mean particle size $1.2 \mu\text{m}$, much larger than those without densification ($0.3 \mu\text{m}$). Therefore, this powder looks much more coarse than other powders. Furthermore, particles of this powder do not show big hollow centers because the evaporation of solvent through the coarse surface is easy and the ballooning of droplets during spray-drying is not obvious. This powder has a mean particle size and bulk density $18.2 \mu\text{m}$ and 1.93 g/cm^3 , respectively.

Fig. 5d shows the powder of SPL19 (3YSZ + 1.8 wt.% PEI + 1 wt.% ethylcellulose). Most of the particles are not spherical and cotton-like induced by the swelling-up or crack of cellulose. The mean particle size and bulk density of this powder are $7.3 \mu\text{m}$ and 1.27 g/cm^3 , respectively.

4. Conclusion

The controlling factor of the property of spray-dried powders is the suspension preparation. In order to prepare a powder with high density, large particle size and good flowability, the solid content in the suspension should be high enough, and the starting powder should be densified at an appropriate temperature before drying if it is porous. For the application of spray-dried powders in plasma-spray coating, PEI is a good binder.

Acknowledgements

The authors thank Mr. A. Gupta and Dr. W. Fisher for SEM analyses.

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