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# Underwater Plasma Processing of Stabilized Zirconia for Thermal Barrier Coatings

*E. Lugscheider and I. Rass*

**The influence of powder technology on the spraying process is growing. The use of powders of different morphologies results in a variety of coating properties. Plasma processing of ceramic composite powders underwater produces dense and spherical powders with excellent morphologies. Coatings of improved quality are produced by spraying these powders. This paper describes the concept of producing zirconia powders by a plasma process that is performed underwater. The most important parameters and standards are highlighted. Moreover, the influence of powder characteristics on coating properties will be described and some results presented.**

## 1. Introduction

PRESENTLY, thermal barrier coatings (TBC) have centered on the use of zirconia for thermally loaded components. The advantages of zirconia include low thermal conductivity and good thermal shock resistance.[1] For high-temperature applications (> 1000 °C), zirconia must be stabilized with other metal oxides. The addition of cubic stabilized oxides such as MgO, CaO, $Y_2O_3$, or $CeO_2$ increases the stability range of the cubic and tetragonal crystallographic forms of zirconia from room temperature to quite high temperatures. In this way, the detrimental volume expansion (5 to 6%) that takes place at the tetragonal to the monoclinic phase change[1,2] can be avoided, and the service life of stabilized zirconia coatings can be improved considerably. Zirconia powders are mainly used in the partially stabilized (PSZ) phase for the thermal spraying of thermal barrier coatings. These powders are typically manufactured by the following processes—fusing and crushing, spray drying and sintering, or sintering and plasma treating.

Each of the powder characteristics influences the plasma spraying process and the resulting coating properties. Two of the most important powder characteristics are flow behavior and particle grain size range. A powder that flows well results in powders being fed continuously into the plasma without pulsing. A narrow particle size range prevents inhomogeneous melting of the particles in the plasma. Also, these particles can be injected much better into the center of the plasma. These specific requirements enable criteria for powder production to be established. On the one hand, there is the need for reproducibility and reliability of the powder production process, and on the other, a powder with defined characteristics must be guaranteed for coating production. It is apparent that this concept of the plasma production of powders is not limited to ceramic materials, but can also be extended to multicomponent powders. Multicomponent powders based on several metallic components have been manufactured and sprayed. The powders exhibited improved properties, such as high density and excellent flow characteristics, which lead to dense coatings with high deposition efficiencies. These coatings also exhibit improved wear resistance.[3]

An additional feature is that the plasma processing concept of powder production opens a new field for sintering and hot isostatic pressing (HIP) technology where powders that flow well are required. The realization of composite powders containing integrated signaling elements as "intelligent materials" provides interesting aspects for future work. The extension of powder plasma processing in an underwater environment where plasma is immersed in water offers some advantages. For example, the cooling effect of water (rapid quench) allows materials to be processed so that no solid or solution solubility results. The powder process is also very efficient with virtually no waste, because all the powder particles are recovered at the end of the process. Further advantages are the reduction of noise, radiation, and dust due to the isolation of the process under water, and thus, there is no need for an exhaust system.

The authors center their discussion on a plasma processing technology for the production of spherical powders in a defined particle size range. The authors also discuss the influence of process parameters on powder characteristics.

**Key Words:** circular shape factor, powder morphology, powder processing, thermal barrier coatings, underwater plasma, zirconia powders, circular shape factor

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## 2. Objectives and Performance of Investigation

These investigations dealt with the production of powder with known characteristics. Moreover, the reproducibility and reliability of the powder production should be guaranteed. These objectives were achieved by specifying the following characteristics: well-defined particle size distribution, high flowability, no residual moisture, low porosity, high mechanical strength, high apparent density, and high grade of stabilization.

These requirements are precisely defined and, in fact, mandated in industrial powder specifications such as from original engine manufacturers, *e.g.*, Rolls Royce, Pratt & Whitney, and General Electric. The qualitative and quantitative measurements of these characteristics were made with the following techniques.

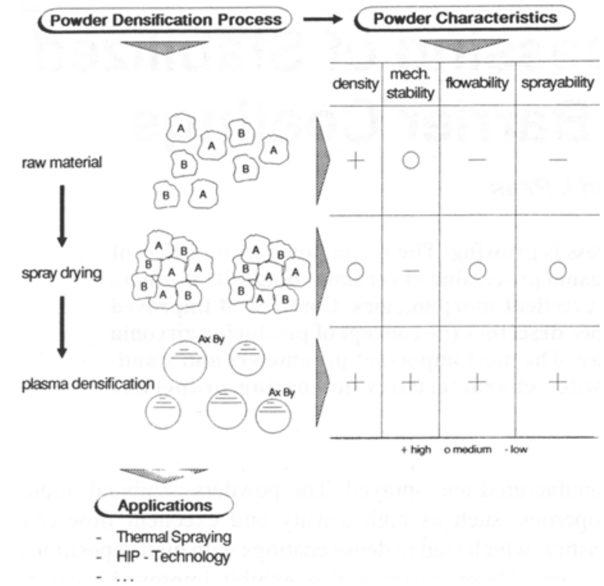


**Figure 1** Schematic of underwater plasma processing of composite powders. The different material components are indicated either as A and B (when in the form of solids), or as $A_x$ and $B_y$ (when in solution).

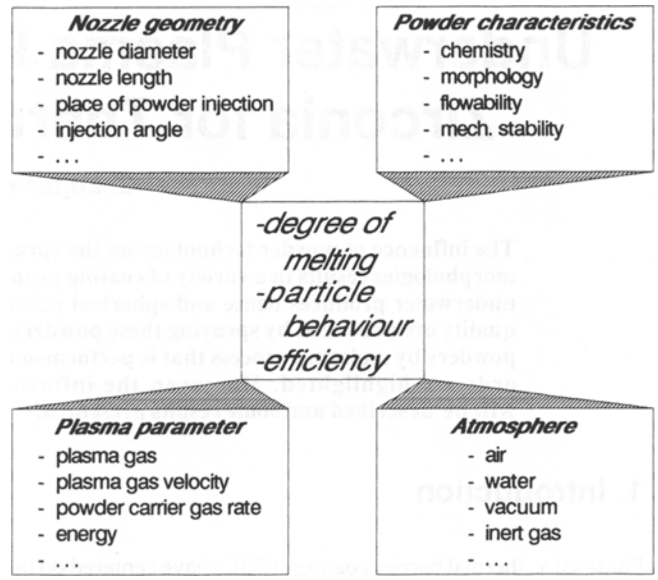


**Figure 2** Specific characteristics of powder plasma processing.

Particle size and particle size distribution were determined with a computer-aided characterization system (IBAS 2000), sedimentation (Sedigraph 5000 ET), and standard sieve analysis. The geometric shape form of particles was ascertained with the IBAS 2000 system. The circular shape factor (CIRSF) is defined as DCIRCL = 2 · (specific area of particle/π)$^{0.5}$. A material that is perfectly spherical can be characterized with a CIRSF of unity. The material density was measured by gas pycnometry (Accupyc 1330) and liquid pyonometry (using a liquid dibutylphatalat). The apparent density was measured according to the ISO 3923 standard.[4]

The rheological (or flow) characteristics of the powders were determined by the Hall flow meter method according to ISO 4490, DIN 4490.[5] The morphology of the powder includes the shape, porosity, and structure of the powder particles, and these characteristics were ascertained qualitatively by scanning electron microscopy (SEM). The SEM and IBAS 2000 instruments were also used to determine the degree of melting. X-ray diffraction (XRD) enabled phase determination and hence the degree of stabilization to be measured.

The terminology used in the field of powder metallurgy is defined in ISO 3252, DIN 30 900[6] and ASTM designation B243-88.[7] The sampling of powders was performed in accordance with DIN (ISO) 3954.[8]

## 3. Plasma Processing of Multi-Component Powders Under Water

The powder production process consists of spray drying, a sintering process and then plasma densification (Fig. 1). The feed material for the spray drying process is $ZrO_2$ mixed with $Y_2O_3$, MgO or $CeO_2$, water, and an organic binder (polyvinyl alcohol). This mixture is dispersed in droplet form into a drying chamber, where it comes in contact with hot gas. The liquid carrier is evaporated, and the dry product is recovered. Spherical particles are produced that vary in size from fine to coarse by controlling the operating variables. These particles have a homogeneous distribution of the participating elements within the particles. The sintering step that follows is necessary to increase the strength of the spray-dried powders. Thus, a preliminary heat treatment enables partial consolidation of the particles so that they do not burst in the plasma due to mechanical and thermal loads. Agglomerated powders are not suitable for plasma spraying, because their low density causes them to be very fragile. Moreover, the high power of the plasma jet (up to 55 kW) causes agglomerated zirconia particles to break up in flight and, therefore, results in very poor deposit efficiencies. Thus, it is mandatory to densify such agglomerated particles before spraying, thus obtaining well-densified and spheroidized particles with good flow characteristics.

The particles are injected into a plasma, become molten, and then are sprayed directly into water. The underwater plasma densification equipment consists of a water tank, a modified Plasma Technik PT-F4 plasma torch, handling system, power and control unit, and a powder feed unit. Physical environmental conditions are different when densifying powders under water compared to air densification. It is necessary to define certain characteristics to specify the objectives of investigations into underwater plasma densification. These features are defined as particle behavior in the plasma, so that there is no bursting of the agglomerated particles, and process efficiency so that the particle densification rate and particle size generation properties can be optimized. Figure 2 shows the parameters that specifically influence these features.

Two other densification methods have been investigated at the University of Limoges other than the underwater plasma densification method of the Technical University of Aachen. A fluidized bed system allows control of the powder dwell time in

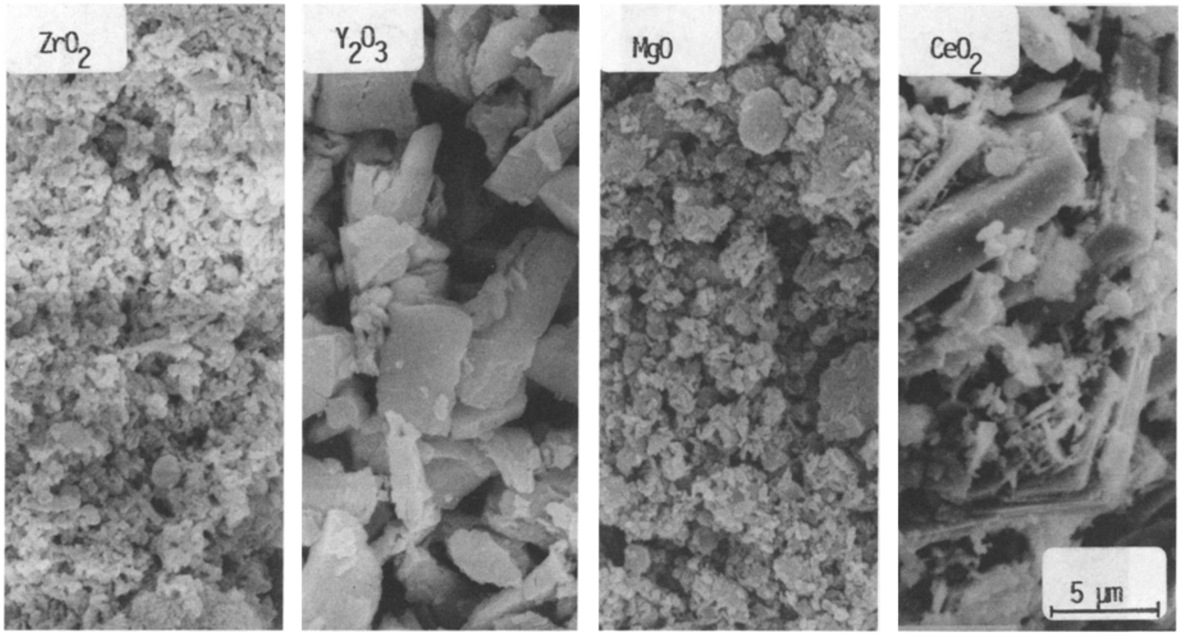


**Figure 3** Morphologies of raw materials for spray drying. All micrographs are at the same magnification. $ZrO_2$ and MgO are coprecipitated powders, whereas $Y_2O_3$ and $CeO_2$ are fused in an electric arc.

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Two other densification methods have been investigated at the University of Limoges other than the underwater plasma densification method of the Technical University of Aachen. A fluidized bed system allows control of the powder dwell time in the plasma fluidized bed. A plasma torch with vortex injection of nitrogen gas at the bottom of the fluidized bed was used. The temperature of the bed can be easily adjusted between 100 and 1800 °C depending on the particle size, densifying gas flow rate, and powder mass flow rate. The other method consists of a transferred arc system for the densification of agglomerated powders. The arc is transferred to a graphite ring to prevent hot particles from sticking. The torch works in a controlled atmosphere chamber using argon and helium as plasma gases.[12] The results of powder production with integrated underwater plasma densification (performed at the Technical University of Aachen) will now be described.

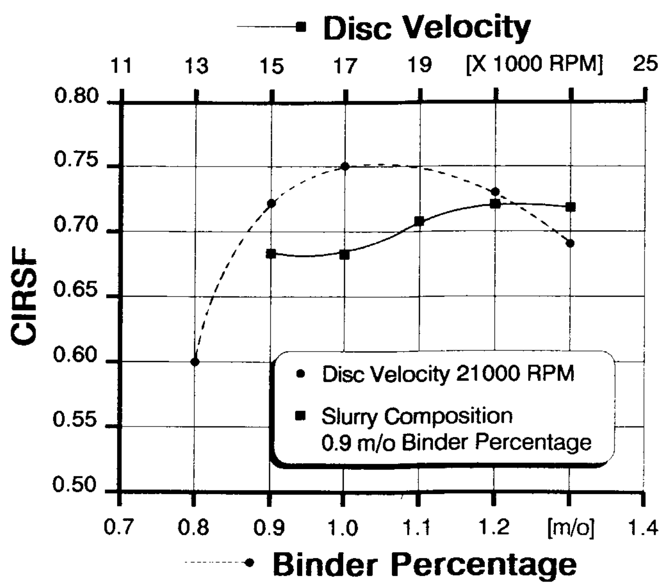


**Figure 4** Circular shape factor (CIRSF) related to binder percentage and disc velocity.[9]

## 4. Results and Discussion

Spray drying is the first step of powder production and requires specific powder characteristics. A sufficient area of contact between the individual particles is necessary to avoid weak bonding of the agglomerates. Moreover, a narrow particle size range is necessary for a homogeneous distribution of the zirconia particles and stabilizing elements in the liquid feed, as well as in the agglomerates. In this case, the mean particle diameters of the raw materials are about 0.3 to 0.5 µm. The raw materials were produced by either precipitation or were fused and crushed. Figure 3 illustrates several powder morphologies for spray drying.

The most critical points of the spray drying process are the optimum balance of water, binder, and powder, as well as the spray drying parameters such as inlet and outlet temperature and

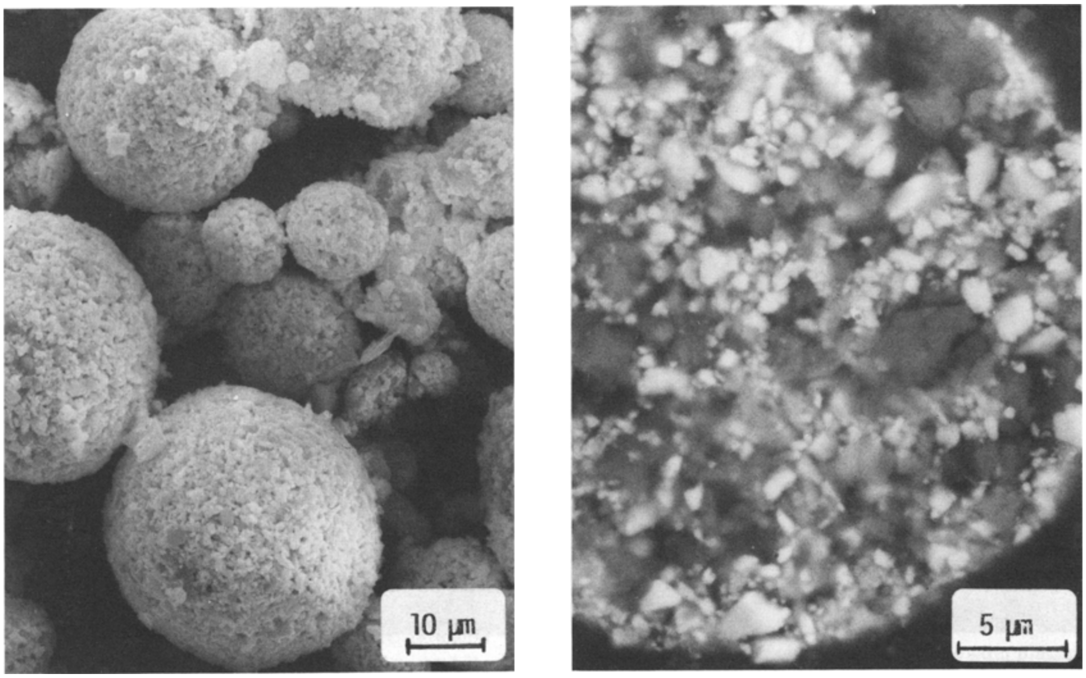


**Figure 5** Morphologies of spray dried $ZrO_2$/MgO 76/24 powder.

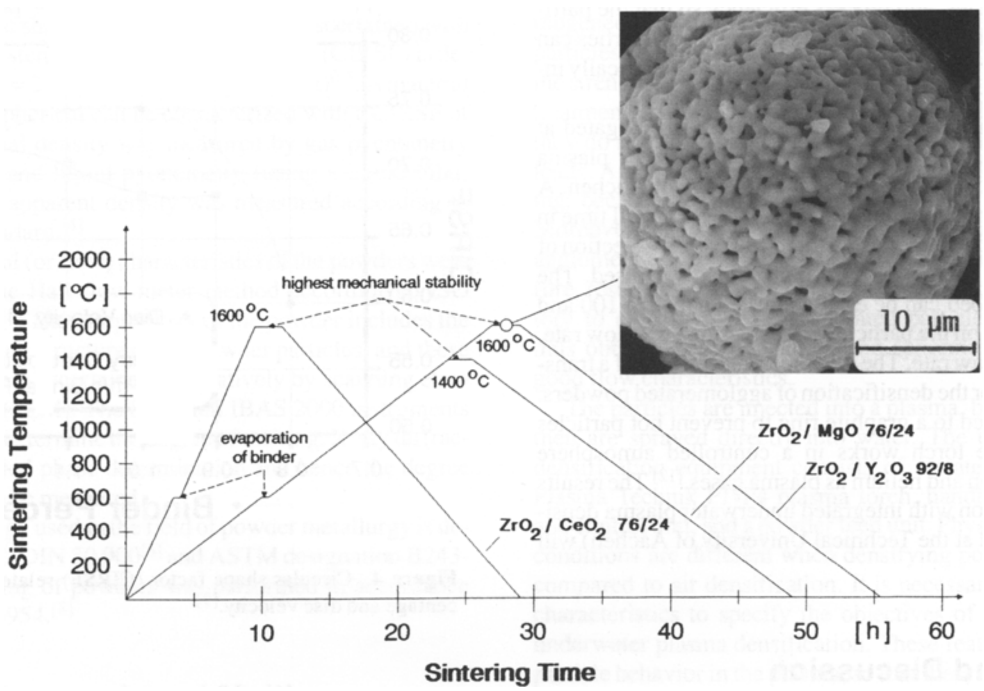


**Figure 6** Heating curves and surface structure of sintered 92 wt.% $ZrO_2$-8 wt.% $Y_2O_3$.[10]

the velocity of the rotating disc. Figure 4 illustrates the correlations between the CIRSF and binder percentage and the speed of rotating disc[9]. The purpose of this study is to define the highest circular shape factor with respect to the binder percent and disc velocity. Measurements of CIRSF range between 0.5 and 0.8. It should be noted that these parameters directly depend on the morphologies of the raw materials. For spray drying of 76 wt.% $ZrO_2$-24 wt.% MgO (MSZ) powder, the highest CIRSF value of

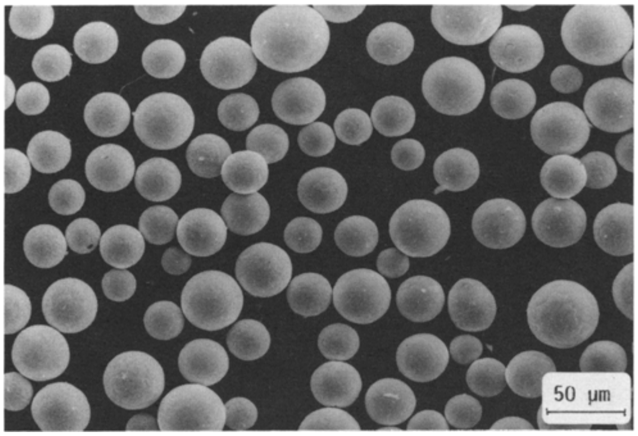

**Figure 7** Morphology of underwater plasma processed 75 wt.% $ZrO_2$-25 wt.% $CeO_2$ powder.

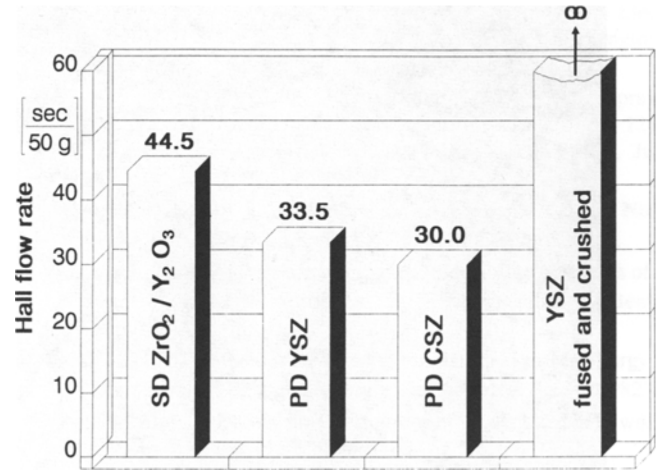


**Figure 8** Hall flow rate of spherical underwater plasma processed powder and blocky fused and crushed powder. "SD" refers to "spray dried" and "PD" refers to "plasma densified."

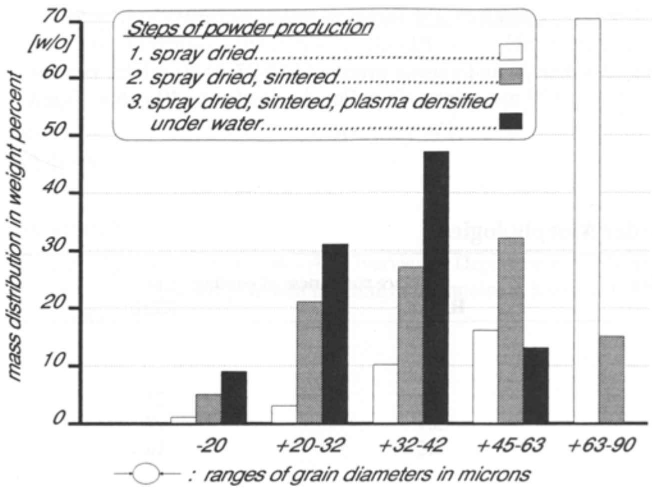


**Figure 9** Particle size distribution of spray dried, sintered, and underwater plasma processed CeSZ 75/25.

0.75 (disc velocity of 21,000 rpm) could be achieved. A reduction of binder percentage from 1 to 0.9% causes lower CIRSF of powder particles, as does varying the disc velocity from 15,000 to 23,000 rpm. Viscosity measurements lead to a good mixture of components with 51 wt.% powder, 48 wt.% water, and 1 wt.% binder. One of the morphologies achieved by spray drying MSZ powders is shown in Fig. 5. The powder particles exhibit a spherical form with their typical rough features. Moreover, a homogeneous distribution of the different materials can be observed.

It should be remembered that these powders are quite friable and break up under mechanical handling, such as during transport with the carrier gas to the plasma flame. Therefore, the spray dried powders are unsuitable for plasma processing and need to be further processed. After spray drying, the powders are sintered. Sintering enables the removal of the binder and also increases the mechanical strength of the particles by oxidation to $CO_2$. The different stages and phenomena of sintering are well described in Ref 10. Retaining optimum flow characteristics during the sintering step is crucial. Heating rate, holding temperatures, and cooling rate must be optimized to achieve these objectives. Figure 6 reveals the heating cycles of different powder types. The inset micrograph features the surface structure of a sintered 92 wt.% $ZrO_2$-8 wt.% $Y_2O_3$ particle. The individual particles of $ZrO_2$ and $Y_2O_3$ are slightly molten as revealed by the well-rounded protuberances on the particles, and this implies an increased mechanical strength of the particle.

The final powder study centered on powders prepared by plasma processing. The powders are injected into a plasma, become molten, and are then sprayed directly into water. The morphology of underwater plasma processed 75 wt.% $ZrO_2$-25 wt.% $CaO_2$ (CeSZ) is shown in Fig. 7. Every powder particle has been molten and reveals a smooth surface with a dense structure. The flow characteristics of the powder are often increased by this step of powder modification. The plasma processed powder exhibits excellent flow behavior (see Fig. 8), whereas the fused and crushed powder with its block particle shape does not flow very well. As mentioned previously, powders for aircraft applications are required to meet powder specifications. These technical requirements include chemical composition, phase structure, and particle size distribution. The production of powders with an estimated particle size ranging from 15 to 60 μm requires raw spray dried powders with larger diameters. This relation is demonstrated in Fig. 9. As shown, most of the spray dried powder of CeSZ falls in a range between 32 and 90 μm. Following underwater plasma processing, the powder structures are densified by particle consolidation, and an estimated particle size range of 15 to 60 μm can be achieved. The powder yield after sieve classification is very high, which suggests that the processing is efficient.

The spherical powders were then sprayed to form coatings. Figure 10 reveals the microstructures of coatings sprayed with spray dried (left) and underwater plasma-processed 75/25 CeSZ. All powders were sprayed with the same plasma spray parameters. The microstructures indicate the influence of powder

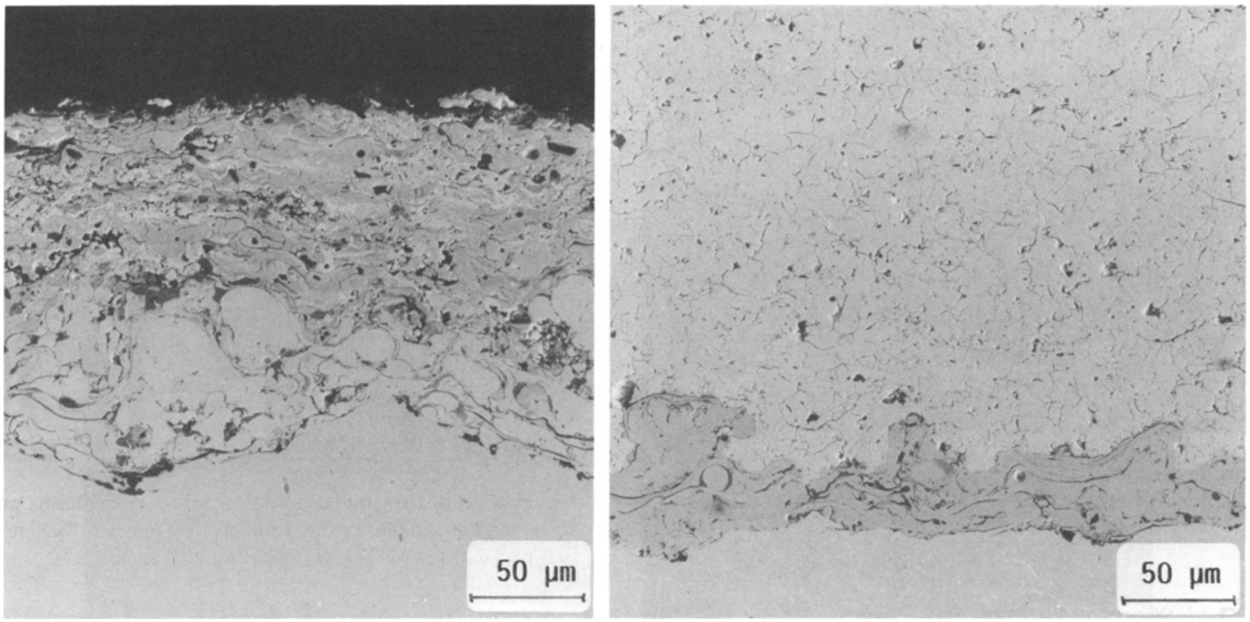


**Figure 10** Microstructures of thermal barrier coatings sprayed with spray dried (left) and plasma-processed CeSZ 75/25 (right) powder. Plasma parameters: 600 A, 56 V, 40 SLPM Ar, 12 SLPM $H_2$. Spraying distance: 120 mm, air cooling. Powder feed rate: 40 g/min. Torch: Plasma-Technik PT-F4.

**Table 1 Characteristics of Coatings Sprayed with Different Powder Morphologies**

| | Deposition efficiencies, % | Surface roughness of coatings, µm RA(a) | RZ(b) |
|---|---|---|---|
| **MSZ** | | | |
| SD | 18 | 5 | 28 |
| SD + SI(d) | 32 | 3.4 | 20 |
| UPD(e) | 49 | 3.2 | 18 |
| YSZ | | | |
| SD | 17 | 5.5 | 29 |
| SD + SI | 41 | 3 | 22 |
| UPD | 58 | 2.8 | 16 |
| CeSZ | | | |
| SD | 18 | 4.9 | 31 |
| SD + SI | 48 | 3.4 | 23 |
| UPD | 80 | 2.5 | 14 |
| fused and crushed | 40 | 4.8 | 28 |

**(a)** Ra: arithmetic mean roughness value. **(b)** Rz: mean peak-to-valley height. **(c)** SD: spray dried. **(d)** SD + SI: spray dried and sintered. **(e)** UPD: underwater plasma densified.

morphologies on the resultant coating quality. Deposition efficiencies of 80% are achieved by spraying plasma-processed spherical CeSZ powders, whereas other morphologies such as fused and crushed, blocky, and irregular forms exhibited deposition efficiencies of up to 40%. Moreover, the surface roughness of plasma-sprayed coatings decreases by spraying plasma-processed powders (see Table 1). Thermal barrier coatings with low surface roughnesses are of technological importance because fuel consumption is reduced. Furthermore, a denser structure is produced that seals and protects the base material against corrosive attack.

The powder production rate described in this work was performed on a laboratory scale. About 2 to 2.5 kg/hr (depending on powder type) can be processed under water. The next step will be to upscale powder production by using more torches simultaneously or by using high energy torches (up to 2000 kW).

## 5 Concluding Remarks

This paper details the production of dense and spherical zirconia powders with specific characteristics to meet aircraft powder specifications for thermal barrier coatings. It introduced the production processes of spray drying, sintering, and underwater plasma densification. The most important parameters for a reproducible and reliable powder production were emphasized. Results were given for powder obtained by the various steps of powder production routes and compared with powder characteristics of fused and crushed Yttrium Stabilized Zirconium (YSZ). Examination of the influence of modified powder characteristics on coating properties underlined the necessity of excellent powder morphology to produce high-quality plasma-sprayed coatings. Moreover, this concept of powder production is not only limited to zirconia powder. Nearly every powder type can be combined, spray dried, and plasma processed. In this way, it is possible to combine the advantages of different materials into one type of composite powder, and it opens a new field of application for powder and plasma technology.

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