Effective parameters in axial injection suspension plasma spray process of alumina-zirconia ceramics

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Suspension Plasma Spray (SPS) is a novel process for producing nano-structured coatings with metastable phases using extra small particles as compared to conventional thermal spraying. Suspension spraying involves, atomization, solvent evaporation and melts consolidation, which can cause substantial complexity in the system. Using feedstock mixtures for composite coatings, such as alumina and zirconia, intricacy of the system increases even more. There is consequently a need to better understand the relationship between plasma spray conditions and resulting coating microstructure and defects. In this study, an alumina/ 8 wt% yittria stabilized zirconia was deposited by axial injection SPS process. The effects of principal deposition parameters on the microstructural features are evaluated by using Taguchi design of experiment (DOE). The microstructural features include micro-cracks, porosities and deposition rate. To better understand the role of the spray parameters, in-flight particle characteristics, i.e. temperature and velocity were also measured. The role of the porosity in this multi-component structure is studied as well. The results indicate that thermal diffusivity of the coatings, an important property for potential thermal barrier applications, is barely affected by the changes in porosity.

1 Introduction

Suspension plasma spray (SPS) is an emerging process for spraying small feedstock particles with nano and or a few micron range size, using a liquid carrier. These particles are mostly less than 5 µm dimension and are difficult to feed using conventional equipment, since they tend to form larger aggregates that can cause blocking the injection path. Injection of such particles into a plasma jet can be achieved with the help of liquid carriers. The resulting microstructure favors dense or finely porous structures as needed for solid oxide fuel cell electrolytes [1] or cathodes [2]. Moreover, more investigation is required for better controlling the range of porosity and other structural features obtainable with this process. SPS can generate unique and novel microstructure, not commonly seen in conventional thermal spraying [3] and understanding the role of the process parameters, which impart these microstructural features, has increasing importance.

In addition, the feedstock size and size distribution also play an important role, as well as the nature of the material. Using multi-component feed materials increases the difficulty of producing uniform microstructures in the coatings, for example, mixtures of alumina and yittria stabilized zirconia. One reason is the effect of combination of molten particle/substrate material on splat shape and morphology [4] that may continue in the following layers with alternating material (e.g. alumina or zirconia layers of the composite coating) and result in unexpected splat behavior as compared with a substrate of a single material. Meanwhile, substrate condition is another important process parameter in the coating studies.

This study was conducted to identify the significant process parameters including plasma torch, feed and substrate in producing a reliable microstructure. Such a structure is required for future studies of the characteristic properties of the coating produced by suspension plasma spray process. For this study the eutectic composition of alumina/ 8wt%yittria stabilized zirconia was used.

2 Experimental

2.1 Liquid Feed Material

To produce two different powder size ranges, 3 mol% YSZ (Nano-Composite Powder, Inframat@ Advanced Materials; Farmington, USA Nominal size 30-60 nm) and 8 mol% YSZ (Nano-Composite Powder, Inframat@ Advanced Materials; Farmington, USA, size 30-60 nm) nano-powders were proportionally mixed to produce 8wt% YSZ, which is the common thermal barrier coating (TBC) material in gas turbines and diesel engines. The resulting doped zirconia powders were then mixed with two different sizes of alumina powders. The alumina component was nano sized (Nanostructured & amorphous Materials Inc. USA, Nominal size 27-43nm) or micron sized (Malakoff, Texas, USA, size 1.4 µm). The former mixture was called "Nano" and the latter "Micron". The mixture with the larger sized powder was ball milled in a concentrated suspension of 60% solid for 24 hours before dilution to the final solid concentration. This procedure ensured homogeneous mixing and stabilization of the suspension. The nano mixture was milled for the same period for enhanced stability of the suspension.
A weight ratio of 60/40 for the alumina/ 8 wt% YSZ were prepared and suspended in ethanol at 10 and 30 wt% concentrations. This resulted in four suspensions with different powder size ranges and solid contents.

Suspension dispersion was done by using 9cc (Polyethylene-imine) and 4.5cc (Nitric acid) (both with 10% concentration) for every 150 g of solids. Wet analysis of the suspension was performed by infrared Culter-Beckman particle size analyzer to determine the size of agglomerated solid particles in the suspension.

2.2 Methodology

The spray system Mettech Axial III torch (Northwest Mettech, North Vancouver, Canada) was used. This torch consists of three cathodes and three anodes that can reduce the average arc voltage fluctuations. The injection system is fully automated and PC controlled to ensure a constant feed rate, which can have significant effects on the spray process and the resulting coatings.

The spray distance was kept constant at 50 mm, as short spray distances are commonly used in SPS [5, 6]. In-flight particle characteristics (velocity and temperature) were monitored by diagnostic system Accura-Spray G2 (Tecnar Automation, St. Bruno, Canada). This system measures particle temperature and velocity based on ensemble particles signals rather than the signal from individual particles. The measurements were taken at the substrate position.

FE-SEM (Hitachi S4700) was used to image the coating microstructure. SEM (Jeol JSM-610) was utilized in Image Analysis (IA) at 500X magnification and the average porosity was determined from measurements in 10 locations. Calibration thresholds were selected between two reference materials, namely aluminum foil and the mounting material. This method is useful for large porosities in the coating; it is, however, limited to detect the porosities less than 0.5 μm at this magnification [7].

The vertical and horizontal cracks that are sometimes reported as a part of total porosity are individually assessed and counted per unit length or width of the coating. Five measurements were averaged per sample. The nature of the cracks can have significant influence on the properties of the coating. For example, it was observed that the planar defects were more influential than total porosity on mechanical properties [8] as well as thermal diffusivity [8, 9]. Thermal diffusivity was evaluated by a laser flash method [10].

The statistical method of Taguchi was used to evaluate the importance of seven selected variables in the SPS coatings, including feed, plasma torch condition and substrate related variables. The need to investigate a wide range of variables with the minimum number of experimental runs provoked the application of this DOE (Design of experiment) [11].

The variables and their two selected values (levels) are summarized in Table 1.

The microstructural features and in-flight particle characteristics on which the effects of variables are being studied were:

- Particle temperature, T_p, at impact distance (°C).
- Particle velocity at impact distance, V_p, (m/s).
- Vertical cracks average spacing (μm).
- Horizontal cracks average spacing (μm).
- Porosity content in the crack-free area (%).
- Thickness per pass of deposition or deposition rate (μm /pass).

Table1. Variables and Levels

Variable		Low& high levels
A	Solid content in suspension	10 & 30 wt%
B	Auxiliary gas	H_2 & He
C	Torch condition (total plasma gas flow, gas composition, torch current)	(245slm, 75Ar/10N_2/15 auxilary gas, 200 A) & (275 slm, 65Ar/15N_2/20 auxiliray gas, 240 A)
D	Injected feed rate	1.3 & 1.8 kg/hr
E	Powder type	Nano & Micron
F	Substrate roughness	#24 & #60 mesh size of alumina for grit blasting
G	Spraying robot travel speed	24 & 80 in/s

3 Results and Discussions

3.1 Suspension Agglomerate Size Distribution

The wet analyses of the agglomerate size in different suspensions diluted in water were closely comparable regardless of the initial particle size or solid concentrations and are all in the range bellow 10 μm. That is 0.2~3 μm in 30% solid of micron sized particle suspension, 0.2~9 μm in 10% solid of the same powder and 0.2~5 μm in nano sized powder in 10% solid suspension.

3.2 Effects of the Variables

A summary of the results of Taguchi evaluations are imaged in bar chart graphs in Fig.1. The first column for every variable shows the effect of its variation from the low level to high level as defined in Table 1. The second column for each variable is the standard error to help comparison of the significance of the effects with the error.
When changing the variable (e.g. solid weight%) from low to high level has increased the specific structural parameter (e.g. vertical crack spacing) in the coating, the related column is shown in positive side of the X-axis and the decreasing effects of variables on the measured parameter are shown in negative side of this axis.
By relating the particle temperature and velocity to the spray conditions, some general trends can be observed.

A- Solid Concentration

Increasing the solid content from 10 to 30% in the suspension liquid, based on the results in Fig.1, has decreased both particle temperature and velocity. The coating from this lower temperature and velocity have shown no considerable change in vertical crack density but it experienced a slight increase in the spacing of horizontal cracks through the thickness.
Within the precision of the method used in this experience, the porosity content of the coatings was not

affected by the solid concentration. It however, shows to be the most effective factor on deposition rate. The higher solid content in the liquid feed has produced thicker layers per pass, which can be translated to the higher rate of material deposition. It can also be reasoned that thicker splats are a result of lower T_p, causing higher droplet viscosity, and lower V_p, causing lower momentum for deformation, both of which could reduce the splat flattening.

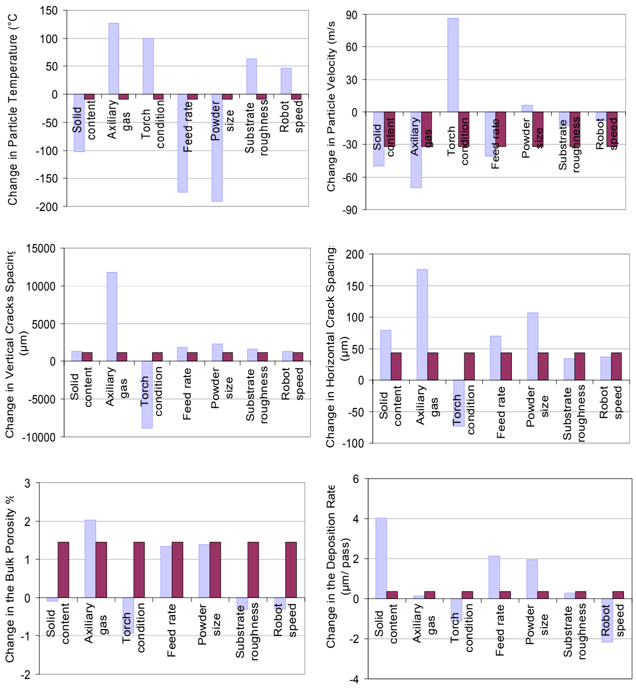

Fig.1. The averaged effects of the seven variables on particle characteristics and microstructural parameters in suspension plasma spray (SPS) process

B- Plasma Auxiliary Gas

Changing the plasma auxiliary gas from commonly used hydrogen to helium, was implemented to induce more porous microstructures for applications like thermal barrier coatings. Helium is known to increase the plasma stability with its higher viscosity at high temperature [5]. It also has a higher conductivity than Argon and generally produces wider hot core area that promotes entrapment of larger number of small particles, which could otherwise escape from the particle jet without deposition.

Interestingly the transfer from hydrogen to helium auxiliary gas has shown the most drastic effect on almost all of the measured parameters in this experiment. This experiment using the Taguchi method has shown that by replacing H_2 as auxiliary plasma gas with He gas, the average particle temperature increases and the average velocity decreases. One by one comparison, however, gives some more information that may be extracted from Fig.2.

Fig. 2 shows that at the same plasma torch condition (in terms of total gas flow rate, plasma gases ratio and arc current) application of He has dropped the resulting plasma power by 20 to 40 kW. This can be observed in two different plasma condition of "245 slm total gas flow rate, 75Ar/10N_2/15 auxiliary gas, 200 A current" and "275 slm total gas flow rate, 65Ar/15N_2/20 auxiliary gas, 240 A current".

On the other hand comparison of the two sets of experiments in Fig. 2 clearly shows that application of He auxiliary gas resulted in both higher velocity and temperature of the in-flight particles, even though only small differences of plasma power around 80-82 and 84-85 KW were recorded. This temperature increase in spite of shorter heat exposure time at higher velocity is a result of higher heat conduction by helium gas.

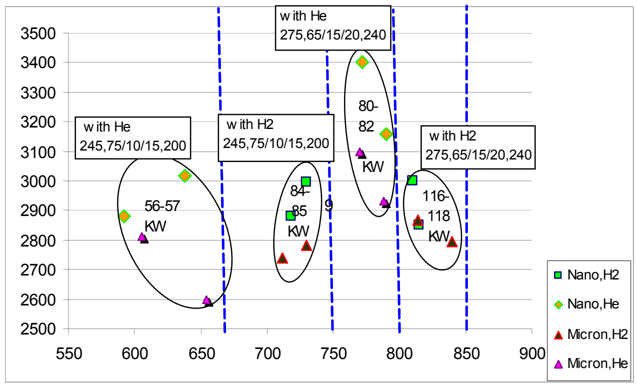

Fig.2. The effect of auxiliary Gas, powder size, torch condition and plasma power on Particle velocity and temperature

The suspension plasma spray (SPS) coatings produced within the range of variables in this experiment show a very dense microstructure. The porosity in crack free areas ranges from a minimum of almost zero, produced with hydrogen auxiliary gas, to a maximum of 8% with helium. The two extreme microstructures of alumina/YSZ coatings are shown in the micrographs of Fig. 3 a, and b. It is clear that while the high density of the coating in Fig. 3 c causes the vertical microcracks to develop within the structure, the porous structure, especially in case of distributed porosities as in Fig. 3 d, eliminates the microcracks.

A comparison of the particles temperatures and velocities indicated on the micrographs as (T_p, V_p) shows that for high densities a high particle velocity is necessary.

C- Plasma Torch Condition

Changing the plasma condition from the low to high level as described in Table 1 and based on the results in the graphs of Fig. 1 raised the particle temperature and, to an even higher degree, the particle velocity.

At higher particle temperature and velocity the density of both vertical and horizontal cracks increases. The reason is probably in the formation of thinner splats that can more readily form vertical cracks during the cooling process. The horizontal cracks branch from the vertical cracks. In this way the similar behavior from both types of cracks may also be justified. The porosity remains invariant and the deposition rate decreases slightly. A direct comparison, however, is difficult since the parameters of spray torch condition and auxiliary gas are not independent. To gain further insight into the effect, deposition runs can be grouped into four ranges of plasma power of 56-57, 80-82, 84-85 and 116-118 kW.

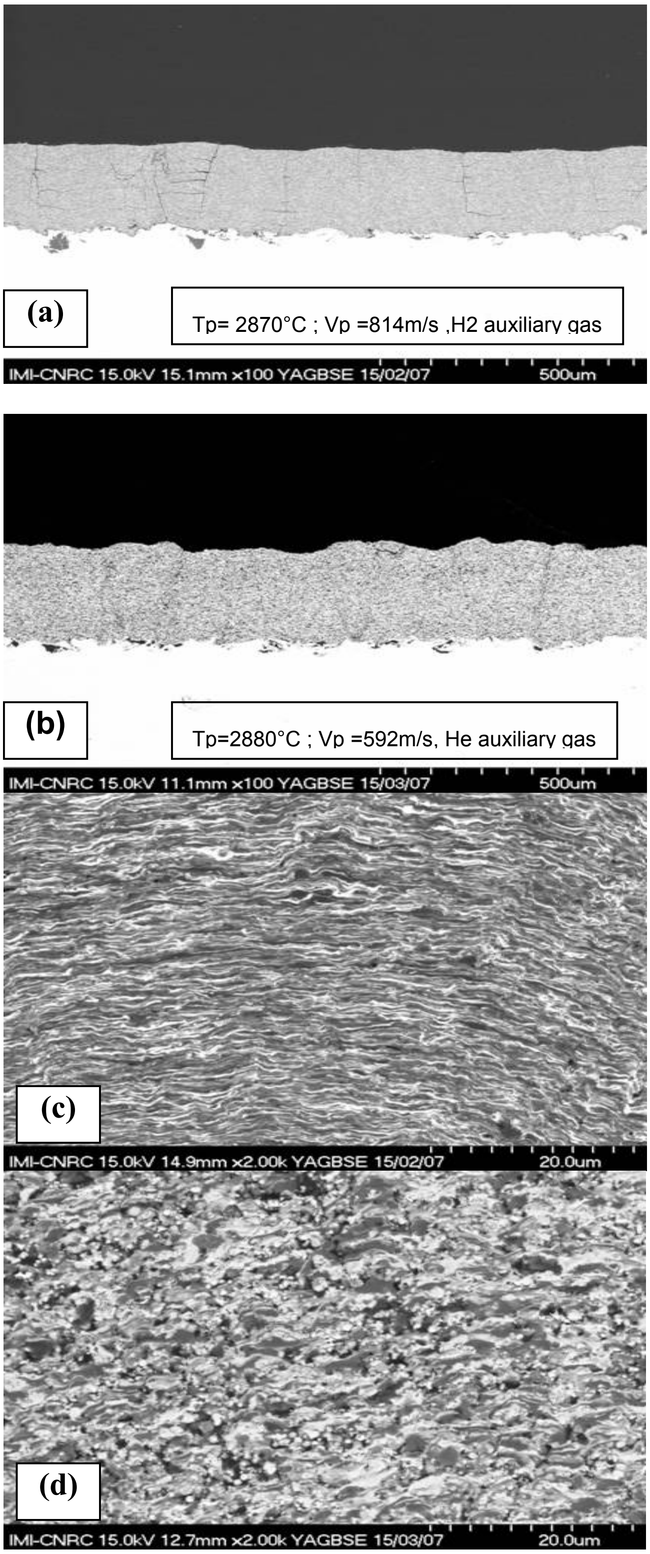

Fig.3. 60/40 wt% alumina/zirconia suspension plasma sprayed coatings a, b) coatings at 100X. c, d) Same coatings as a, b, respectively at 2KX

Accordingly the effect of different plasma input powers on the particle characteristics is summarized in Fig. 4. It can be seen that an increase in plasma power generally increases the particle velocity. At similar plasma power (81-84 kW), particle velocity in helium exceeds that in hydrogen as in Fig.4 a. Nonetheless, the highest particle velocities are attained with hydrogen.

As a result of the above condition the average porosity increased with helium and both vertical and horizontal cracks spacing show an increasing trend. The deposition rate was indifferent to this change.

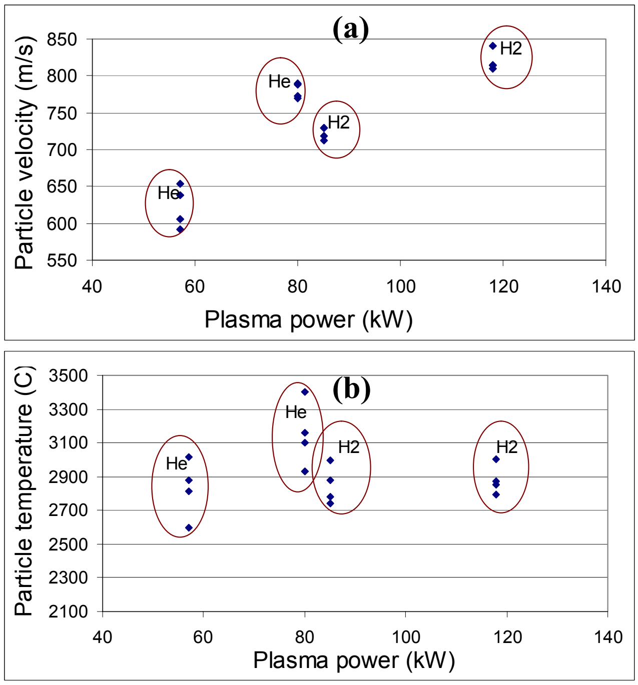

Fig.4. Plasma power effect on (a) particle velocity and (b) particle temperature

The temperature of the particles, however, does not follow a definitive trend, as seen in Fig.4 b. Generally, it was observed that the feed parameters are better tools for variation of particle temperature than the torch operating parameters.

D- Feed Rate

Based on the Taguchi analysis, increasing feed rate decreases both particle temperature and to a lesser extend particle velocity.

As a result the microcracks density does not show any considerable change. The porosity also did not get affected by this change.

This characteristic of the process that can tolerate the increase of the feed rate and deposition rate without introducing more structural defects in the coating is promising for higher production rates.

It is noteworthy that the feed rate and the solid content have shown similar effects and maybe interchangeably used in controlling the coating microstructure in SPS process.

E- Powder Size Distribution

The change in the initial particle size range was done by changing nano to micron size alumina powders mixed with nano size 8wt% yttria stabilized zirconia. This variation showed a recurring drop in particle temperature (T_p) in spite of the similar agglomerate size in the suspension. No significant velocity drop occurred. The lower temperature from larger particle feedstock may be explained by the formation of dense particles within the plasma plume in comparison with hollow particles, which can result from nano-size suspension feedstock [12]. A second reason for higher (T_p) can be that the nano particles that form loose aggregates are of considerably higher surface area thus lower energy barrier for melting than solid micron sized particles in the aggregates. Experiencing the same velocity and spray distance, the nano aggregates, more rapidly melted, can rise to higher temperatures.
In the resulting coating microstructure the average porosity presented no change and while the density of vertical micro cracks remained almost constant the horizontal microcrack spacing increased remarkably.
The lower microcrack densities observed with larger particles can also be justified by the lower $T_{p,}$ as the high particle temperatures can cause higher thermal stresses.
The porosity content looks indifferent to the powder size variation. This is somewhat unexpected. Considering the large standard error, a possible underlying effect may not be captured. The limited sensitivity of the porosity measurement method also has restricted the observation of the smaller pores (nano-pores) that might have varied the results.

F- Substrate roughness

Keeping in mind that the substrate roughness has no effect on in-flight particle characteristics, this experiment shows that its variation is one of the least effective parameters on the microstructural features, as seen in Fig. 1. Neither the porosity nor the deposition rate has changed, and even the microcrack densities (vertical/ horizontal) have not altered, as compared with the standard error.
Additionally, the averages of coating roughness on the #60 and #24 alumina grit blasted substrates are almost the same, namely, 5.5 and 6 µm, respectively. The absence of strict correlation between the initial substrate roughness and the resulting coatings suggests that the coating roughness can be controlled by spray condition for various substrate roughnesses. On the other hand the initial particle size change from nano to micron size powders in the suspension causes a slightly more considerable effect on coating roughness, namely, from 5.1 to 6.3 µm.

G- Robot Travel Speed

Increasing the robot travel speed, again not having any effect on particle state, has neither changed the porosity nor vertical/horizontal microcracks density. A drop in deposition rate is simply related to less mass deposition time at higher robot travel speed.

3.3 Porosity and Thermal Diffusivity

A group of samples with a range of minimum and maximum porosities obtained were evaluated for thermal diffusivity. The results are summarized in Fig.5. A porosity of 0 to 8 percent in the crack free area obtained in this experience has not altered the thermal diffusivity of the coating.

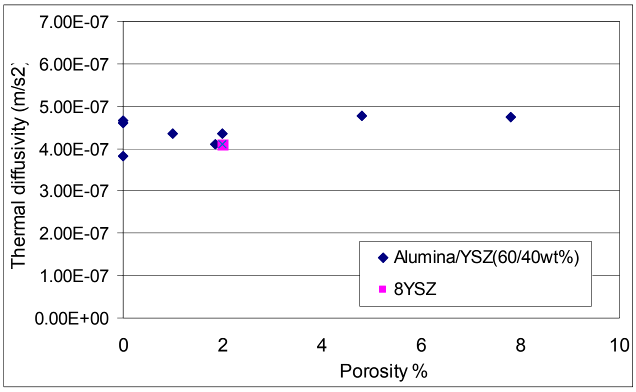

Fig.5. The variation of Thermal Diffusivity with the Porosity content

The measured thermal diffusivities of the coatings are, however, comparable with that of the stabilized zirconia sprayed with the same process. It is noteworthy that the thermal conductivity of the 8 wt% yttria stabilized zirconia formed by this process was calculated as 0.89 W/m°C. This value is in turn comparable to values reported in the literature [14] for air plasma sprayed YSZ (0.9~1 W/m°C) and YSZ deposited by EB-PVD (Electron beam physical vapor deposition) in the order of 1.8~2 W/m°C.
This result may reduce the significance of porosity content for thermal barrier application. In this way the implementation of dense composite coating can promote the potentially better mechanical properties.

4 Summary and Conclusion

In this study the importance of some key variables in suspension plasma spraying of multi-component alumina/stabilized zirconia coatings was evaluated.

It was observed that the variables that directly affect the particle velocity and temperature were the most influential on the microstructure. Considering the greater significance of particle velocity in this regard, variables with more prominent effect on V_p were of prime importance.

On the other hand, the substrate and robot related variables that play any role on neither T_p nor V_p, did not consequently affect the coating microstructure.
It was experienced that for variations in particle velocity, the plasma torch parameters e.g. total gas flow and plasma gas composition were most important. On the other hand, particle temperature is more readily manipulated by feed parameters like solid content, particle size and feed rate.

Helium auxiliary gas was successfully used as a tool to achieve a wider microstructural variety in the SPS coatings. It especially helped introducing higher porosity content in the coating.
Thermal diffusivity in SPS coating for multi-component system of 60alumina /40YSZ is reasonably low and does not change with bulk porosity of up to 8%.

5. Literature

[1] C. Delbos, C. Rat, C. Bonhomme, J. Fazilleau, J.F. Coudert, P. Fauchais, Influence of powder size distributions on microstructural features of finely structured plasma sprayed coatings, High Temperature Material Processes 8 (2004) 397-406.

[2] C. Monterrubio-Badillo, H. Ageorges, T. hartier, J. F. Codert, P. Fauchais, Plasma spraying of a perovskite suspension for SOFC cathodes, Proceedings of the 2003 International Thermal Spray Conference: Advancing the science & applying the technology, ASM International, Materials Park, Ohaio, USA. 687-692

[3] S. Siegmann, N. Margadant, A. Zagorski, M. Arana-Antelo, Composition of particle in-flight-characteristics and coating properties, Proceedings of the 2003 International Thermal Spray Conference: Advancing the science & applying the technology, ASM International, Materials Park, Ohaio, USA (2003) 1591-1598.

[4] C.J. Li, W.B. Wang, A. Ohmori, K. Tani, Relationship between the microstructure and properties of thermally sprayed deposits, Proceeding of the 15th Thermal Spray Conference, Nice, France, vol.1, 481-487

[5] C. Delbos, J. Fazilleau, V Rat, JF Coudert, P. Fauchais, B Pateyron, Phenomena Involved in Suspension Plasma Spraying Part 2: Zirconia Particle Treatment and Coating Formation, Plasma Chemistry and Plasma Processing (2006)26, 393-414

[6] P. Fauchais, V. Rat, C. Delbos, J.F. Coudert, T. Chartier, L. Bianchi, Understanding of suspension DC plasma spraying of finely structured coatings for SOFC, IEEE Transactions on Plasma Science 33 (2005) 920-930

[7] S. Deshpande, A. Kulkarni, S. Sampath, H. Herman, Application of image analysis for characterization of porosity in thermal spray coatings and correlation with small angle neutron scattering, Surface and Coatings Technology 187 (2004/10/1) 6-16.

[8] C- Li, A. Ohmori, Relationship between the microstructure and properties of thermally sprayed deposits, Journal of Thermal Spray Technology 11 (2002) 365-374.

[9] F. Cernuschi, P. Bianchi, M. Leoni, P. Scardi, Reviewed Papers - Thermal Diffusivity/Microstructure Relationship in Y-PSZ Thermal Barrier Coatings, Journal of Thermal Spray Technology 8 (1999) 102-109.

[10] A.S. Houlbert, P. Cielo, C. Moreau, M. Lamontagne, Measurement of thermal diffusivity and anisotropy of plasma-sprayed coatings, International Journal of Thermophysics 15 (1994) 525-546

[11] Box,G.-E.-P.; Hunter,W.-G.; Hunter,J.-S. ,Statistics for experimenters an introduction to design, data analysis, and model buildings, John Willey & Sons Inc., Canada1978

[12] R. Vassen, F. Traeger, D. Stover, Correlation between spraying conditions and microcrack density and their influence on thermal cycling life of thermal barrier coatings, Journal of Thermal Spray Technology 13 (2004) 396-404.

[13] J. Oberste Berghaus, J.G. Legoux, C. Moreau, F. Tarasi, T. Chraska, Mechanical and thermal transport properties of suspension thermal sprayed alumina-zirconia composite coatings, Journal of thermal spray technology, 17(1) March 2008

[14] U. Schulz, C. Leyens, K. Fritscher, M. Peters, B. Saruhan-Brings, O. Lavigne, Some recent trends in research and technology of advanced thermal barrier coatings, Aerospace Science and Technology 7 (2003/1) 73-80.