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Production of Samarium Doped-Ceria Plasma Sprayed Nano-Coatings Using an Internal Injection of a Suspension Containing Nanoparticles

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Thin coatings were produced by plasma spraying using nanoparticles of samarium-doped ceria (SDC) in suspension. For solid fuel cell application, thin electrolyte is needed for novel materials that allow reducing their operating temperature. The influence of what called 'the thermal management of the coating and the substrate' is discussed. In peticular, influence of substrate temperature and the nature of the substrate. It was found that adequate control of the coating and substrate temperature, together with an equivalent substrate/coating thermal expansion coefficients (CTE) are the key-factor to successfully obtain an SDC nanosized thin and dense coating free of cracks.

1 Introduction

Although discovered in the 19th century, the technology of fuel cells (FCs) is still under development (new and cheaper materials and processes) and considered as a future promising pollution-free power generation. Among fuel cells, the Solid Oxide Fuel Cells (SOFCs) present significant advantages. Indeed, it allows an ecologically friendly cogeneration of heat and electrical power, it also has a fuel flexibility and a higher overall fuel to electric efficiency than other FCs.

The SOFCs operate at high temperature, typically around 900-1000 °C. In order to reduce the component cost, research efforts at the moment are focusing in reducing the operating temperature from high to intermediate temperature, ranging from 650 to 800 °C [1-3] and even lower. This would drastically lower the material costs for components like the interconnector and the insulation. This should be accomplished without lowering of the electrochemical and mass transport properties. Traditionnal materials like yttria stabilized zirconia (YSZ), largely used as electrolyte, have a high resistivity towards ionic current at intermediate temperatures; thus, SOFCs using this electrolyte material have to be operated at temperature of 900 °C and higher. An alternative will be to work with new materials having higher conductivity at lower temperatures like gadolinium or samarium-doped ceria ceramics (CGO or SDC). A second alternative consists in compensating the reduction of ionic conductivity when temperature is reduced by the fabrication of a thin electrolyte layer, which reduces the traveling distance for oxygen ions to reach the anode side of the cell.

Fabrication of thin electrolyte layer using traditionnal processes like CVD (chemical vapor deposition), EVD (electrochemical vapor deposition) and sputtering, are still pricey justifying therefore the necessity of using more cost-effective technique such as plasma spraying. The attractiveness of air plasma spray is due to its high deposition rate, low cost and easy masking for deposition of patterned structures compared to traditional film formation processes. Moreover, this approch does not need post heat treatment, and hence, it could be considered as a means of reducing manufacturing cost.

However, conventional plasma spraying processes normally require 10-100 micrometer particle diameter to produce coatings. During spraying, as the molten particles impinge on a surface, they flatten by a factor of 5 to 10. The thickness of produced coatings is about few tens of micrometers, which renders the fabrication of thin electrolyte film impractical. If finer particles are used, it will then be possible to produce finer lamellas. However, particles that have a size smaller than 5 micrometers are almost impossible to feed consistantly onto plasma. The use of a liquid carrying small particles could be a potential solution. There are multiple groups that claim originality on suspension spraying: Amongst others, early work done at University of New York at Stony Brook and at the University of Limoge, where it has been shown the feasibility of using both the internal [4], and external injection [5-9] system of a liquid precursor feedstocks. Indeed, nanosized particles or submicron grained materials in suspension could constitute a liquid droplet with adequate momentum to be propelled towards the substrate. As the heat of the plasma vaporizes the suspension solvent, nanoparticles are agglomerated, densified, melted, accelerated to be flatten and then solidified to form splats. It is then possible to obtain thin coatings with nanosized grains, which are known to have a higher ionic contribution due to the enhancement of anionic vacancy mobility through the large number of grain boundaries.

This study aims at producing thin and nanostructured SDC electrolytes for a planar SOFC with suspension plasma spraying technology, which has unique advantages for this application. The fabrication process will involve external and internal injection adapted to DC Air Plasma. Process conditions will be optimized.

2 Materials and Experimental Details

Samarium-doped ceria ($Sm_{0.2}Ce_{0.8}O_{1.9-x}$< 20nm) is from microcoating (became nGimat, Atlanta GA, USA). This powder was put in suspension and sprayed using two plasma torches: a UPS F4 (Sulzer Metco, Westbury, NY, USA) for external injection and the Mettech III (Northwest Mettech Corp., B.C., Canada) for axial injection.

The prototype system for injection the nanoparticles in suspension was developed in our lab and described in other papers [10,11].

Two types of substrates were used: mild steel and ferritic stainless steels substrates. The second is named Crofer 22 APU (ThyssenKrupp VDM GmbH, Germany), a material developed as an interconnect for

SOFC applications, which has a low coefficient of thermal expansion (CTE) mismatch with SDC materials and presents a low chromia evaporation rate. Substrates have rectangular shape and are 25 mm length, 19.2 mm width and approximately 1 mm thick. Polished and grit blasted substrate were used.
A special sample-holder was designed and built allowing heating the substrates before spraying and rapidly cooling them down to room temperature after spraying.
The diagnostic system (Accura Spray, Tecnar Automation, St.-Bruno, Québec, Canada) was employed to determine the average in-flight temperature and velocity during spraying.
The starting powder and coatings were examined using a field emission scanning electron microscope (Model S4700, Hitachi Instruments Inc., Tokyo, Japan). The microscope was operated in the backscattered and secondary electron modes. Before SEM observations, all coatings, were entirely vacuum impregnated in epoxy resin, cut in the middle, vacuum impregnated in epoxy resin a second time before finally been polished. These steps insure to avoid creating cracks during cutting and polishing procedures.
Porosity levels were assessed by image analysis (Visilog from Noesis, Les Ulis, France). X-ray diffraction measurements were carried out using a Bruker-AXS diffractometer with Cu-K_α radiation. From XRD spectra, the Sherrer method was used to calculate the crystallite size of all coatings.

3. Suspension and Injection System

Suspension stability tests were conducted to investigate effect of different solvents and dilution agents together with different powder concentrations. For this work, 10 wt.% or 5 wt.% concentration of SDC in ethanol was used. Details regarding the suspension stability will be out of the scope of this paper. However, the results showed that the suspension stability varied upon variation of above mentioned parameters but at least the suspension remained globally, under stirring, well dispersed for one day, a time that was jugged sufficient for the different manipulation and hence no more optimization were pursued.
Two different injection systems were built; one is an external suspension injection adapted for the F4 torch and the second is an internal injection system where suspension is fed axially into the Mettech III torch. Detail descriptions of the system as well as effects of the suspension injection parameters were studied and presented in another publication [10,11]. The best suspension injection parameters that have been established from these studies were used here for the SDC coating production.

4. Plasma Spraying

Two kinds of coatings were deposited onto different substrates using in one case, the F4 torch and in the other the axial Mettech III torch. **Table 1** presents some of the tested spray conditions that were used.

Table 1. Sets of plasma spray parameters used for the F4 (a) and the Mettech III (b) torches, respectively.

(a)

Plasma Parameter Set		F-1	F-2	F-3
Primary Gas Ar	(SLPM)	35	50	50
Secondary Gas H_2	(SLPM)	10	14	14
Arc Current	(A)	500	600	600
Output Power	(kW)	24.5	32.6	32.6
Substrate Temperature		Low	Low	High
Spraying Distance	(cm)	5	5	5

(b)

Plasma Parameter Set		M-1*	M-2*	M-3*
Total Gas Flow Rate	(SLPM)	120	180	245
Primary Gas Ar	(%)	10	45	75
Secondary Gas N_2	(%)	80	45	10
Secondary Gas H_2	(%)	10	10	15
Arc Current	(A)	160	180	200
Output Power	(kW)	73	85	82
Spraying Distance	(cm)	5	5	5

* For example, coating will be named M-1-A, M-3-A or M-3-B...depending on their substrate temperature.

5 Results and Discussion

5.1 Spraying with the F4 Torch

First SDC coatings have been produced with the F4 torch using the external injection suspension system. The major issue regarding this kind of injection is the ability for the suspension to penetrate into the plasma jet. The velocity of the droplets at the nozzle exit is the key-factor to feed them consistently into the plasma without either, crossing the jet from one side to another or not penetrating the plasma jet due to a lack of momentum.

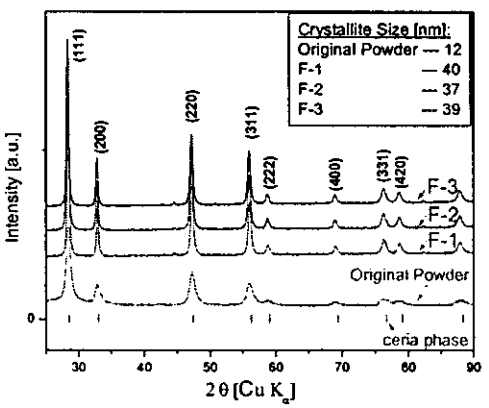

Fig. 1. X-ray diffraction patterns of the starting feedstock and the produced coatings described in **Table 1a**.

Fig. 1. shows the X-ray diffraction patterns for all tested coatings sprayed using the F4 plasma torch. XRD analysis indicates that, as in the case of the starting feedstock, the as-sprayed coatings display the major reflection of fluorite structure of ceria and all exhibit a high level of crystallinity. Thus, original phase

composition is retained. Moreover, independently of thermal spray conditions, SDC coatings stay in the nanostructure form. Indeed, the crystallite sizes of all the coatings stay below 40 nm.

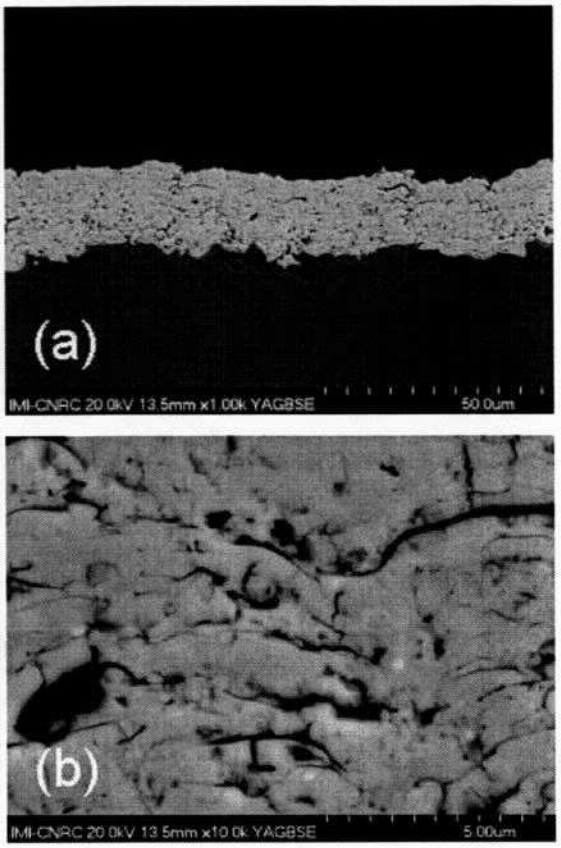

Fig. 2. SEM cross-section images for coating F-1 described in Table 1: at low (1k) (a) and high (10k) (b) magnifications.

Fig. 2a. shows an image of a coating cross-section produced by using the plasma condition F-1 with 10% SDC as suspension concentration. It is clear that the process is able to successfully produce a thin coating. Indeed, the coating has a thickness of 25 μm and presents relatively well-melted lamellas necessary to obtain a dense coating. However, it exhibits a relatively bad splats cohesion (**Fig. 2b.**), which gives the impression of porous-like coating structure. Better intersplat cohesion could be achieved by a higher particle temperature and velocity, as will be shown in the next section.

5.2 Spraying with the Mettech III Torch

To overcome the difficulty for a suspension to penetrate into the plasma jet, a direct injection of the powders into the center of the plasma was envisaged. For this purpose the Mettech III has been used to feed the suspension in the center of three converging plasma jets, giving all particles a best chance to be fully entrained in the plasma. Moreover, this torch allows achieving a high in-flight particle velocity approaching those obtained with an HVOF gun.

5.2.1 Effect of Plasma Spray Conditions

An attempt was made to measure the in-flight particle velocity and temperature of the SDC material. Due to possibly high optical transparency and/or high evaporation rate of this material at high temperature, it was not possible to measure those parameters. An indirect way to proceed has been used to rank in-flight particle velocity and temperature associated with each of the four sets of plasma parameters given in **Table 1b**. Indeed, by using a zirconia nanopowder, instead of the SDC one, sprayed with the same sets of plasma spray parameters, it was possible to associate a couple (T, V) to each set [11]. It is obvious that these values will be different for the SDC nanopowders. However, these results were used to rank the in-flight particle velocity and temperature obtained in these plasma conditions.

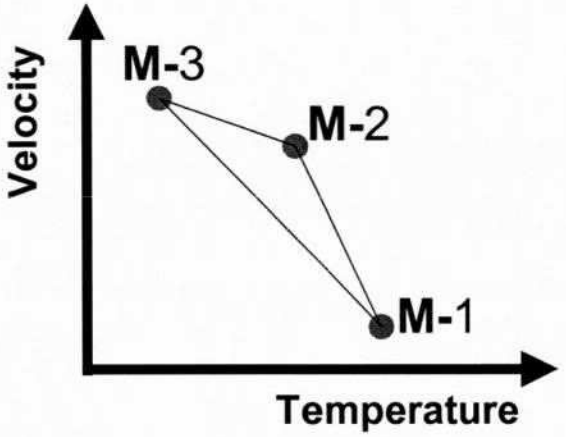

Fig. 3. Ranking of the in-flight SDC particle velocity and temperature obtained when using the plasma spray conditions described in **Table 1b**.

As schematically shown in **Fig. 3.**, coatings M-3 were produced with conditions given the highest in-flight particle velocity and lowest temperature, while coatings M-1, on the contrary, were produced with conditions that generate the highest temperature and the lowest velocity.

This range of parameters allows producing different structures. **Fig. 4.** shows a coating (M-1-A) produced with plasma spray set M-1 and 10% SDC as suspension concentration, which exhibits a high porosity resulting from a low in-flight particle and cold substrate temperature of 120 °C. The coating structure presents a relatively high portion of non-melted and/or resolidified spheroidized particles. It is noteworthy that this kind of structure is sought for the anode and electrode fabrication. Delbos et al. reported a very similar microstructure in zirconia at a low plasma enthalpy and velocity [9]. This group attributed the large porosity they have found to a large number of particles, melted and already solidified, trapped by bigger particles still being in plastic state. The large horizontal crack that can be seen between the coating and the

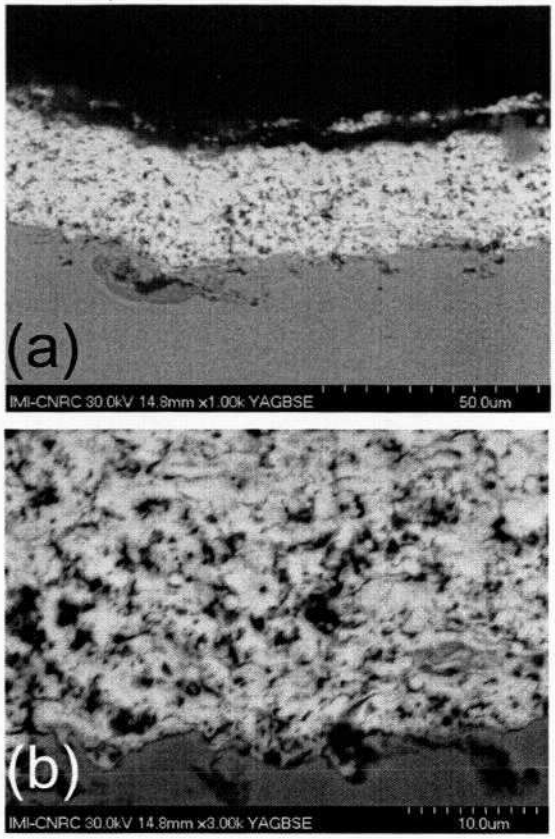

Fig. 4. SEM cross-section images for coating M-1-A at low (1k) (a) and high (3k) (b) magnifications.

epoxy is extrinsic to the coating quality. It resulted from tensile stress exercised by the shrinking epoxy on such thin coating.

The increase of the in-flight particle velocity with the M-2 plasma condition set with 10% SDC as suspension concentration, together with a relatively high substrate temperature ($T_s \approx 370$ °C), produced the coating M-2-B, which is denser than the previous one **(Fig. 5.).** However, this coating still exhibits a porous structure and not a sufficiently good splat bonding. Poorly densified surface and less coherent structure attributed to low surface temperatures were also observed for alumina [10] and zirconia [11-13]. Thus, a higher substrate temperature should helping in obtaining a more dense coating.

Denser coatings where obtained with plasma parameter set M-3, which in addition to the highest in-flight particle velocity, also produced with highest substrate temperatures, i.e. 370 and 595°C for coatings presented in **Fig. 6a.** (M-3-B) and **6b.** (M-3-C), respectively. Both coatings were sprayed using 10% SDC as suspension concentration. Nevertheless, although the second coating seems denser, it exhibits vertical cracks likely formed due to an increasing sample tensile stress.

At this point, a better understanding of phenomena responsible for the coating crack generation should be pointed out.

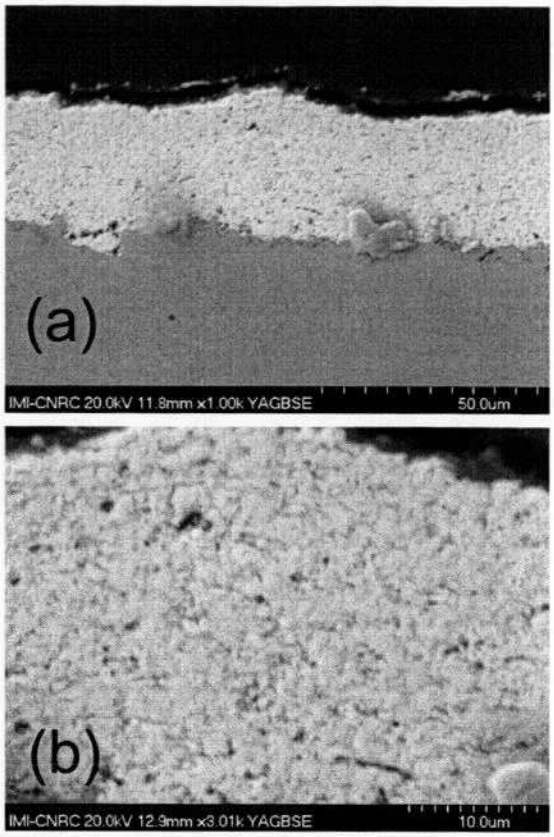

Fig. 5. SEM cross-section images for coating M-2-B at low (1k) (a) and high (3k) (b) magnifications.

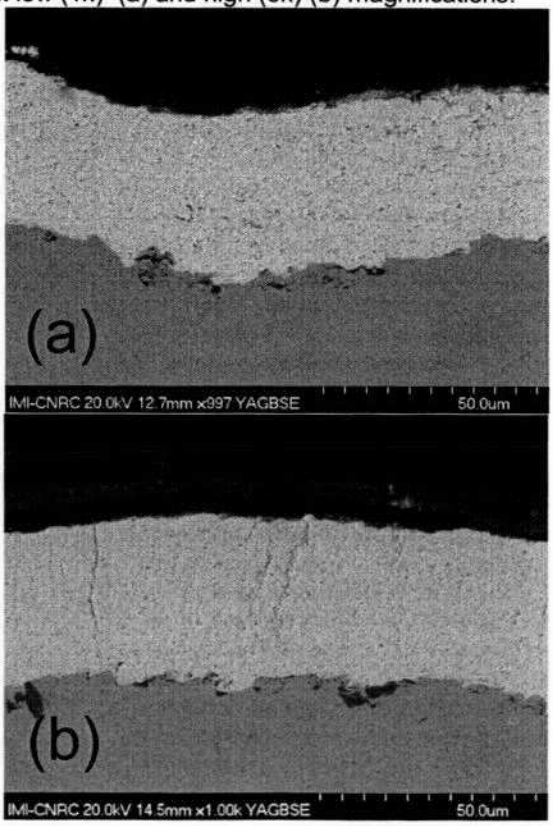

Fig. 6. SEM cross-section images for coatings M-3-B (a) and M-3-C (b), respectively.

5.2.2 Coating/Substrate Thermal Management

In general, due to the high temperatures associated with thermal spray processes and differences in CTEs between the coating material and the substrate material, residual stresses in the coatings are unavoidable. Residual stress on coatings was reported in many publications [14-17]. Generally, two stress components can be distinguished: quenching stress and thermal stress due to the different CTEs. The first one is generated during building up the coating with deposited splats and could be described by equation (1),

$$\sigma_q = \alpha_c (T_m - T_s) E_c \quad , \qquad (1)$$

where α_c , T_m , T_s and E_c are the coating CTE, lamella melting temperature, substrate temperature and coating Young's modulus, respectively. Because the lamella temperature is higher than the substrate temperature, the quenching stress is always tensile and decreases with the increase of the substrate temperature. Rigid coating (high elastic modulus) also produces high tensile stress.

The second source of residual stress is the thermal stress that is generated when cooling the coating at room temperature and is mostly dependant on thermal coefficient mismatch between the coating and the substrate. Equation (2) [17] describes it.

$$\sigma_{cooling} = \frac{(\alpha_c - \alpha_s)(T_d - T_r) E_c}{1 + 2\left(\frac{E_c t_c}{E_s t_s}\right)} , \qquad (2)$$

where α_s , T_d , T_r , t_c , t_s and E_s are the substrate coefficient of thermal expansion, deposit temperature, room temperature, coating and substrate thickness and substrate Young's modulus, respectively. If, as the temperature decreases, the coating is contracting more than the substrate ($\alpha_c > \alpha_s$), tensile stress is generated. At the opposit, if the substrate is contracting more than the coating ($\alpha_c < \alpha_s$), the cooling stress is compressive. The final overall stress is the addition of quenching and cooling stresses. This is of course do no takes into account others stress that might be generated by other effects like penning or grit blasting, which is known to severely cold work the substrate and inflicts it with compressive stress[18].

For SOFC application, all the cell component must mechanically withstand the thermal stress of the heating and cooling cycles experienced during operation at relativelly intermediate or high temperatures. Moreover, the coating should be dense and crack free to ensure the gas tightness necessary for the electrolyte component. A key-factor for the successful deposition of the electrolyte is the thermal management of the sample (deposit/substrate). Indeed, from one hand, the interconnect over which, successivelly the anode then the electrolyte will be coated, should have a similar CTE as the two cited components (that is the reason of using the crofer 22 APU, a good candidate as interconnect material for intermediate temperature SOFC). On the other hand, one would target minimizing as much as possible the sample stress. This is possible by modulating the cooling stress to negate the quenching stress and even render the overall residual stress compressive.

Given that, and from equation 2, the thermal management of the system dictates cooling more the substrate than the coating and spraying thinner coatings. Thus, theoretically the coating final stress could be modulated to be compressive or the least possible tensile stress. Another factors that should be taken into account for designing the final stress; not sufficient high deposit (coating/substrate) temperature would result on a bad splat adhesion and also, spraying a thicker coating will increase tensile stress.

In light of the above-mentioned points, to control the stress evolution, a special sample-holder was designed and fabricated. It allows heating the substrate up to 700 °C and cooling it down to room temperature with a high heat transfer rate. The application of this thermal management procedure allowed the production of relatively high dense coatings with porosity lower than 1.5% (M-3-D in **Fig. 7.**). Indeed, the microstructure at high magnification (**Fig. 7c.**) does not show any open porosity and no visible splat boundaries that could indicate a bad intersplat cohesion. Better interlamellar contacts is necessary to get a good ionic conductivity of the SDC electrolyte [19]. It is interesting to observe also in **Fig. 7c.** special structures, indicated by arrows and called here 'gray zones', appearing like pores without being so. It is believed here that these structures is constituted by unmelted particles or low density SDC materials. In order to verify this hypothesis, a suspension with a higher SDC concentration was sprayed with the same plasma spray conditions and substrate temperature. **Fig. 8.** shows the corresponding coating structure (M-3-E). It can be clearly distinguished that this later structure exhibits much more of the 'gray zones' and presents less dense structure. Contrary to the coating shown in **Fig. 7c.**, this later was sprayed using a suspension with SDC concentration of 10 wt.% instead of the 5 wt.%. It is becoming clear here that lower concentration is required to obtain a denser structure. Similar observations were also reported in another work presented by our group [10]. This is in accordance to what stated by Siegert et al. [20] who noted that the coating density is strongly influenced by the amount of overspray particles (unmelted particles), and by Delbos et al. [7] who indicated that lower suspension concentration favors better spreading of the due to a better thermal transfer and an enhanced momentum transfer.

When using a concentration of 5wt.% of SDC in the solvent instead of 10 wt.%, the deposition efficiencies (DE) are much higher, possibly because of loading effect. DE is in the order of 20% for suspension concentration of 10wt.% SDC and 30-50% for suspension concentration of 5wt.% SDC.

Finally, it is worthy to mention that, as in the case of the F4 torch, all as-produced coatings presented the same ceria solid solution phase similar to the original feedstock material (**Fig. 9.**). The crystallite size remained below 60 nm in all coatings.

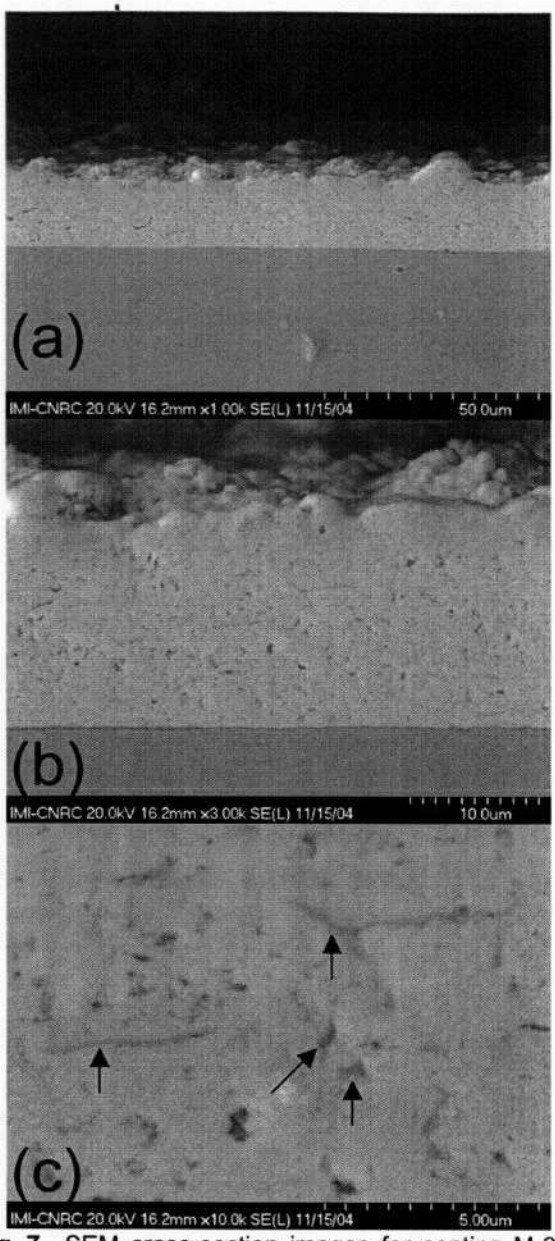

Fig. 7. SEM cross-section images for coating M-3-D at (1k) (a), 3k (b) and 10k (c) magnifications, respectively.

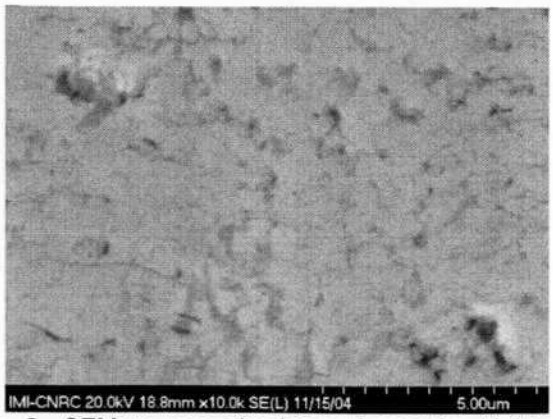

Fig. 8. SEM cross-section image for coating M-3-E.

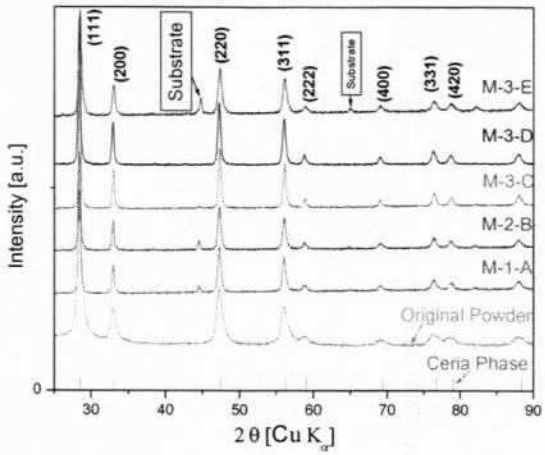

Fig. 9. X-ray diffraction patterns of the starting feedstock and the produced coatings M-1-A, M-2-B, M-3-(C, D and E), sprayed with plasma parameter sets described in Table 1b.

5 Conclusions

This work showed that:

-It is possible to produce thin SDC films by DC plasma spraying using a suspension of nanoparticles. Original phase composition is retained and independently of thermal spray conditions SDC coatings stay in the nanostructure form.

-Depending on plasma spray parameters and substrate temperature, the process can produce a wide variety of structures ranging from porous to dense coating, with very low open porosity.

-A better control of the coating/substrate thermal management associated with an appropriate substrate nature (lowering the CTE mismatch with the coating) are necessary to avoid cracks that are due to an increasing tensile stress with high substrate temperature conditions. The later is unavoidable to obtain the fully dense structure.

The coatings presented here were deposited on small substrate areas. Therefore, the thermal management was relatively easy. It will be interesting and challenging to transfer and adapt the thermal management to coat larger sample. Work is in progress to produce coatings on different substrate sizes and shapes as well as on porous structures.

Acknowledgment

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6 Literature

[1] Huijsmans J.P.P., F.P.F. Van Berkel and G. M. Christie. Journal of Power Sources 71 (1998), Issue 1-2, pp. 107/110.

[2] Stephanie S.J.A., J.W. Cotton and O.R. Mark. Journal of Power Sources 86 (2000), Issue 1-2, pp.411/416.
[3] Yamamoto O. Electrochimica Acta 45 (2000) Issue 15-16, pp. 2423/2435.
[4] Karthikeyan J., C. C. Berndt, S. Reddy, J.-Y. Wang, A. H. King and H. Herman. J. Am. Ceram. Soc. 81 (1998), Issue 1, pp. 121/128.
[5] Wittmann K., F. Blein, J.F. Coudert and P. Fauchais. Thermal Spray 2001: New Surfaces for a New Millennium, (Ed.) C. C. Berndt, K. A. Khor and E. F. Lugscheider, Published by SM International, Materials Park, Ohio, USA, 2001, pp. 375/381.
[6] Wittmann K., F. Blein, J. Fazilleau, J.F. Coudert and P. Fauchais. International Thermal Spray Conference. Conference Proceedings, (Ed.) E. F. Lugscheider, Published by SM International, Materials Park, Ohio, USA, 2002, pp. 519/522.
[7] Delbos C., J. Fazillau, J.-F. Coudert, P. Fauchais, L. Bianchi and K. Wittmann-Ténèze. Thermal Spray 2003: Advancing the Science & Applying the Technology, (Ed.) C. Moreau and B. Marple, Published by SM International, Materials Park, Ohio, USA, 2003, pp. 661/669.
[8] Monterrubio-Badilo C., H. Ageorges, T. Chartier, J.-F. Coudert and P. Fauchais. Thermal Spray 2003: Advancing the Science & Applying the Technology, (Ed.) C. Moreau and B. Marple, Published by SM International, Materials Park, Ohio, USA, 2003, pp. 687/692.
[9] Delbos C., J. Fazilleau, V. Rat, J.F. Coudert, P. Fauchais and L. Bianchi. *Finely structured ceramic coatings elaborated by liquid suspension injection in a DC plasma jet.* Thermal Spray 2004: Advances in Technology and Application: Proceedings of the International Thermal Spray Conference, (Ed.) E. F. Lugscheider , Published by Verlag für Schweissen und verwandte Verfahren DVS-Verlag GmbH, Düsseldorf/Germany., 2004.
[10] J. Oberste-Berghaus, S. Bouaricha, J.-G. Legoux and C. Moreau. Injection conditions and in-flight particle state in suspension plasma spraying of alumina and zirconia nano-ceramics. Submitted for ITSC 2005, Basel, Switzerland.
[11] J. Oberste-Berghaus, S. Bouaricha, J.-G. Legoux, C. Moreau and T. Chràska. Suspension plasma spraying on nano-ceramics using an axial injection torch. Submitted for ITSC 2005, Basel, Switzerland.
[12] Kuroda S. and P. Blazdell. International Thermal Spray Conference. Conference Proceedings, (Ed.) E. F. Lugscheider, Published by SM International, Materials Park, Ohio, USA, 2002, pp. 539/543.
[13] Blazdell P. and S. Kuroda .Surface and Coatings Technology (2000), Issue 123, pp. 239/246.
[14] Hoffman R.W. Physics of Thin Films 3(1966), pp. 211/217.
[15] Clyne T. W. and S.C. Gill. Journal of Thermal Spray Technology 5 (1996) Issue 4, pp. 401/418.
[16] Renault T., M. Vardelle, P. Fauchais, H. Hoffmann and F. Braillard. Thermal Spray 2001: New Surfaces for a New Millennium, (Ed.) C. C. Berndt, K. A. Khor and E. F. Lugscheider, Published by SM International, Materials Park, Ohio, USA, 2001, pp. 743/750.
[17] Stokes, J. and L. Looney. Surface and Coatings Technology (2004), Issue 177-178, pp. 18/23.
[18] Wright R.N. and W.D. Swank. Thermal Spray: Surface Engineering via Applied Research, (Ed.) C. C. Berndt, Published by SM International, Materials Park, Ohio, USA, 2000, pp. 423/428.
[19] Renouard-Vallet G., L. Bianchi, A.L Sauvet, P. Fauchais, M. Vardelle, M. Boulos and F. Gitzhofer. Thermal Spray 2004: Advances in Technology and Application: Proceedings of the International Thermal Spray Conference, (Ed.) E. F. Lugscheider, Published by Verlag für Schweissen und verwandte Verfahren DVS-Verlag GmbH, Düsseldorf/Germany., 2004, pp. 375/381.
[20] Siegert R., J.-E. Döring, J.-L. Marqués, R. Vaßen, D. Sebold, D. Stöver and D. Jülich. *Denser Ceramic Coatings obtained by the Optimization of the Suspension Plasma.* Thermal Spray 2004: Advances in Technology and Application: Proceedings of the International Thermal Spray Conference, (Ed.) E. F. Lugscheider, Published by Verlag für Schweissen und verwandte Verfahren DVS-Verlag GmbH, Düsseldorf/Germany., 2004.