INFLUENCE OF HEAT AND MOMENTUM TRANSFERS BETWEEN THERMAL PLASMA JETS AND STABILIZED ZIRCONIA PARTICULATES ON THE THERMOMECHANICAL PROPERTIES OF THE RESULTING COATINGS

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Résumé

Nous présentons une étude sur des poudres de zircone (stabilisée à l'oxyde d'yttrium) projetées par plasma pour réaliser des barrières thermiques. Nous avons étudié l'influence de la morphologie de la poudre et de sa distribution granulométrique sur les propriétés thermomécaniques des dépôts (dureté, porosité, coefficient de dilatation, diffusivité thermique) et nous avons corrélé les résultats obtenus au traitement thermique de la poudre dans le jet de plasma.

Abstract

This paper presents a study carried out on yttria stabilized zirconia powders with a view to produce thermal barrier coatings. The influence of the powder morphology and grain size distributions as well as plasma jet power level on the thermomechanical properties of the obtained coatings (hardness, porosity, expansion coefficient, thermal diffusivity) is investigated and correlated to the distributions of particle velocity and temperature within the plasma jet.

I - INTRODUCTION

Ceramic thermal barrier coatings (TBCs) deposited by plasma spraying at ambient atmosphere are now widely used in diesel engines, gas turbines and aeroengines. If the conditions of adiabatic engines is by far not yet reached TBCs have extended the service lifetime of the engines, allowed operation with lower quality fuels and reduced the cooling requirements /1 to 3/. In most cases, TBCs consist of a duplex structure composed of a superalloy bondcoat (usually sprayed with the LPPS process) and a 7% wt yttria stabilized zirconia (partially stabilized zirconia : PSZ) coating. However, many works are still under development to improve the mechanical properties and thermal shock resistance of TBCs. These properties, among other parameters, depend on the molten state of the particulates upon impact onto the substrate or the previously deposited layers /4/. The coating is built up particulate by particulate and it has a lamellar structure resulting from the flattening of particulates on already solidified flattened particulates or the substrate. Thus the thermomechanical properties of the coatings depend strongly on the effective contacts between the lamellae and the cracks network resulting from stresses relaxation (stresses induced during spraying or in service conditions). In turn such contacts and cracks network are controlled by :

- heat and momentum transfers to the particulates during their flight in the plasma jet which depend on the plasma jet itself (length, diameter, gas nature, plasma jet surrounding atmosphere), the particle morphology (i.e. the way they are manufactured) and the powder size distribution,
- the way substrate and deposited layers are cooled down and their temperature controlled during spraying.

Up to now the best TBCs (good resistance to thermal shock and destabilization upon service conditions, best mechanical properties) have been obtained when spraying $ZrO_2 - Y_2O_3$

(7% wt) powders with Ar - H₂ dc plasma jets /5 to 12/. Thus this paper is devoted to the study of the influence on the thermomechanical properties (Vickers hardness, porosity, expansion coefficient, thermal diffusivity) of such coatings of the powders morphology (manufacturing process) and size distributions as well as plasma jet power levels. The obtained thermomechanical properties will be linked to the velocity and surface temperature distributions of the particulates in flight controlling their molten state upon impact.

II - EXPERIMENTAL SET-UPS

II.1. Spraying equipment

Deposits are sprayed with a home-made automated set up. The substrates (disk shaped samples $\phi = 20$ mm, $e = 0.5$ mm) are at the periphery of a 120 mm diameter cylinder which axis is orthogonal to that of the torch rotating velocity can be adjusted from 0 to 2880 rpm. The torch movement, parallel to the cylinder axis, is controlled with an Uhing device permitting linear velocities between 0 and 0.4 m/sec. Torch substrate distance can be adjusted between 70 and 150 mm.

The plasma torch used was a home made one with axial gas injection and a cylindrical nozzle whose length is 28 mm and diameter is 8 mm.

II.2. Powder and coating characterizations

The morphology of the particles has been characterized by inspecting their surface or their cross section with either a scanning electron microscope (SEM) or an optical one (OM). Powder size distribution has been controlled by sedigraphy (type 5000 D Micrometric machine) or image analysis working with the 2.2 code of the Olympus Cue 2 image analyser. Their density was determined by the pycnometric method and their crystalline structure by RX diffraction with a Rigaku diffractometer. Mechanical properties have been evaluated considering microhardness measurements with a 5 N load applied during 10 s ; this load has been chosen to evaluate the cohesiveness of the whole deposit and not that of particular grains or lamellae.

Lastly deposit thermal behaviour has been considered with thermal expansion and diffusivity measurements. Thermal expansion measurements have been performed with an Adamei Lhomargy type D10 apparatus with heating and cooling rates of 100°C/hour between 20 and 1500°C. Thermal diffusivity has been measured (with the same heating rate as that for expansion measurements) with the laser flash technique which has been developed at the laboratory by Pawlowsky /13/.

II.3. Particulates in flight

The measuring equipment to follow the particles in flight into the plasma jets consisted of an automated laser doppler or dual focus velocimeter and a two color in-flight pyrometer. Counting the number of particulates passing, during a given time, in one of the focused volume of the laser velocimeter and moving this measurement volume along two orthogonal directions made possible the determination of the particles flux distribution in the plasma jet. A detailed description of the used techniques and apparatus is given in ref. /14/.

III - SPRAYING CONDITIONS

III.1. Plasma torch and spraying distance

Most of the companies spray zirconia particulates by using 6 mm diameter nozzles with typical gas flowrates of 45 slm Ar, 12 slm H₂. For the same gas flowrates, an arc current of 350 A, a shift of the nozzle diameter from 6 mm (83 V) to 8 mm (80 V) results in a decrease of the maximum particulates velocity ($\sim 45 + 10 \mu\text{m ZrO}_2 - 7\% \text{ wt Y}_2\text{O}_3$) from 250 m/s to 200 m/s and correspondingly, for a 80 mm spraying distance, in an increase of the hardness from 550 to 630 HV.

For such a nozzle (8 mm in diameter) two flowrates have been tested : respectively 45 - 15 slm and 75 - 15 slm. Similar hardness values have been obtained with the previous

powders in spite of a higher velocity of the particulates (almost 50 m/s). Such results could be explained by the measurements of M. Vardelle on alumina particulates ($- 21 + 15 \mu\text{m}$) showing that with the higher flowrate the particulates number distribution is better centred along the jet axis with a broader temperature distribution.

Of course these two flowrates have not the same hydrogen percentage (respectively 20 and 17%) but the plasma jet temperature measurements performed by Roumilhac /15/ have shown that if the plasma jet length increases with the H_2 percentage up to 15% it starts to decrease for percentages higher than 20%. This is due to the reduction of the plasma jet viscosity inducing a higher pumping of the surrounding air. Moreover the heat transfer from an Ar - H_2 mixture is almost the same for H_2 percentages between 15 and 20% /16/.

The maximum power level has been limited to 40 kW. Indeed the length of the 50 kW plasma jet is almost identical to that of the 35 kW /15/ due to the increase in surrounding air pumping with the arc current /17/.

For a rotation velocity of the substrate holder of 13.6 m/s and a torch translation velocity of 0.03 m/s, the substrate and coating have been cooled down during spraying with two air jets, one orthogonal to the plasma jet disposed 1 cm in front of the substrate ($13 \text{ m}^3/\text{h}$) and the other flowing at the surface of the sample holders ($4 \text{ m}^3/\text{h}$). In such conditions the coating surface temperature is kept below 160°C during spraying with temperatures gradients of 450 K/mm in the first 0.3 mm.

Spraying at various distances with the $- 45 + 10 \mu\text{m}$ fused and crushed particulates has given the following hardnesses.

Table 1 : Microhardness measurements considering various spraying distances.

Distance (mm)	70	90	110	130	150
HV ₅ N	633	635	521	436	384

Thus finally the retained spraying conditions were the following.

Table 2 : Plasma spraying parameters retained.

Power level	28 kW	40 kW
arc current	350 A	500 A
voltage	~ 80 V	80 V
Plasma gas	Ar- H_2 Ar 70 s1m H_2 15 s1m	
nozzle anode diameter	$8 \cdot 10^{-3} \text{ m}$	
carrier gas	Ar, adjusted to each powder to have the particle mean trajectory as close as possible to the jet axis	
powder flowrate	$0,8 \text{ kg h}^{-1}$ *	
spraying distance	$8 \cdot 10^{-2} \text{ m}$	

* with such a low powder flowrate any load effect is avoided /18/.

III.2. Sprayed powders

Three types of powders, supplied by Herman C. Starck (Berlin) and differing by their manufacturing process, have been evaluated. Three size distributions have been considered and they are presented in the following table :

Table 3 : Powders investigated.

POWDERS WITH ANGULAR SHAPES		POWDERS WITH ROUNDED SHAPES	
Sample number	Sample denomination (and manufacturing process)	Sample number	Sample denomination (and manufacturing process)
1	Zr O ₂ - 7 Y ₂ O ₃ LP (- 90 + 45 µm) (fused and crushed)	7	ZrO ₂ - 7 Y ₂ O ₃ agglomeriert - 90 + 45 µm (agglomerated)
2	Zr O ₂ - 7 Y ₂ O ₃ LP (- 45 + 10 µm) (fused and crushed)	8	ZrO ₂ - 7 Y ₂ O ₃ agglomeriert - 45 + 10 µm (agglomerated)
3	Zr O ₂ - 7 Y ₂ O ₃ LP (GEM PWA 1375) (fused and crushed)	9	ZrO ₂ - 7 Y ₂ O ₃ agglomeriert GEM PWA 1375 (agglomerated)
		10	ZrO ₂ - 7 Y ₂ O ₃ agglomeriert - 90 + 45 µm (agglomerated sintered)
		11	ZrO ₂ - 7 Y ₂ O ₃ agglomeriert - 45 + 10 µm (agglomerated sintered)
		12	ZrO ₂ - 7 Y ₂ O ₃ agglomeriert GEM PWA 1375 (agglomerated sintered)
PWA 1375 corresponds to the specification Pratt and Whitney particle size distribution - 106 + 10 µm			

IV - THERMOMECHANICAL PROPERTIES

Typical results are presented in the following tables.

Table 4 : Microhardness measurements (in parentheses are given measurements after annealings at 1200°C during 100 hours).

Type of powder	size range	Vickers hardness Hv ₅₀₀	
		28 kW	40 kW
fused and crushed	- 160 + 10	505 (760)	589 (791)
	- 90 + 10	375 (715)	466 (786)
	- 45 + 10		612
agglomerated	- 160 + 10	388 (685)	522 (780)
	- 90 + 10	248 (519)	441 (656)
	- 45 + 10		582
agglomerated and sintered	- 160 + 10	434 (642)	453
	- 90 + 10	298 (522)	363 (702)
	- 45 + 10		524

Table 5 : Cristalline structure of deposits (in parentheses are given results on deposits annealed at 1200°C during 72 hours).

Type of powder	size range	predominant phase	other present phase
fused and crushed	- 160 + 10	T (T)	
	- 90 + 10	T (T)	
	- 45 + 10	T (T)	
agglomerated	- 160 + 10	T (T)	M + (M+)
	- 90 + 10	T (T)	M + (M++ at 28 kW)
	- 45 + 10	T (T)	(M+ at 40 kW) M + (M+)
agglomerated and sintered	- 160 + 10	T (T)	(M+ at 28 kW)
	- 90 + 10	T (T)	
	- 45 + 10	T (T)	

The presence of monoclinic phase in the coatings sprayed with agglomerated powders (up to 15% when spraying - 90 + 45 μm particulates at 28 kW) is very detrimental for their service conditions as illustrated by the thermal expansion measurements with agglomerated - 106 + 10 μm particulates sprayed at 40 kW (see fig. 1).

Figure 1 : Expansion measurement of agglomerated powders (- 106 + 10 μm) sprayed at 40 kW.
(a) as sprayed - (b) annealed for 72 hours at 1200°C.

For fused and crushed particulates destabilization occurs at 1350°C when sprayed at 40 kW and at 1300°C for agglomerated and sintered particulates. Thermal diffusivity of as sprayed agglomerated powders are lower than those of agglomerated and sintered ones which are also a bit lower than fused and crushed ones. Fig. 2 shows the values obtained with as sprayed - 106 + 10 μm particulates respectively for fused and crushed particulates and for agglomerated ones.

Figure 2 : Thermal diffusivity of as sprayed - 106 + 10 μm fused and crushed (a) and agglomerated powders (b).

Of course when sprayed at a lower power level in all the cases the diffusivity is lower by almost 15 to 20%. When annealed for 100 h at 1450 $^\circ\text{C}$ (with all the coatings destabilized) the diffusivity of all the coatings becomes the same. This is probably due to the improvement of the interlamellar contacts. When annealed at 1200 $^\circ\text{C}$ slight differences can still be seen.

V - STUDY OF THE PARTICULATES MELTING

V.1. Modelling

Using the temperature distribution measured by Roumilhac /15/, calculating the plasma gas velocity distribution (assuming $V/V_{\text{max}} = 1 - (r/r_{\text{max}})^2$ and determining n and V_{max} by the total gas flowrate and enthalpy conservation) and taking into account the heat propagation phenomenon, it has been possible to determine the temperature evolution of the surface and the center of particulates (depicted in fig. 3) for 30 and 60 μm diameter particulates.

Figure 3 : Surface and center temperature evolution along their mean trajectory of fused and crushed particulates injected in the 29 kW Ar - H₂ plasma jet, respectively for 30 and 60 μm particulates.

It can be seen that, even at the lowest power level, the 30 μm particulates are completely molten while the bigger ones are hardly molten. This is in good agreement with the obtained hardness values (see table 1). It is also interesting to notice that the $106 + 10 \mu\text{m}$ gives much better results than the $-90 + 45 \mu\text{m}$ one. This is due to the presence of small particulates which, even when travelling in the jet fringes, are well molten and help for the contacts between the lamellae.

However the porosity of the powders has also to be taken into account for the heat propagation phenomenon. This is illustrated in fig. 4 where it can be seen that the difference between surface and center temperature is enhanced when a porous particulate (50% porosity) is considered.

Figure 4 : Surface and center temperature evolution versus time for a 60 μm diameter zirconia particulate immersed in an infinite plasma at 10000 K respectively for dense and agglomerated particulates (50% porosity).

V.2. Measurements in flight

They have been performed 75 mm downstream the nozzle exit. Figure 5.a and b show respectively the radial velocity and surface temperature distributions for fused and crushed particulates with the three size ranges in a slice of the plasma jet 75 mm downstream the nozzle exit. As it could be expected, the highest velocities (see figure 5.a) correspond to the smallest particulates. As the measurements are statistical ones, the velocities obtained with the $106 + 10 \mu\text{m}$ are higher than those with the $-90 + 45 \mu\text{m}$ particulates. This is due to the presence of the small particulates that, even when travelling in the periphery of the jet, have higher velocities than the big ones. For the surface temperature (see fig. 5.b), the same tendencies can be observed, the presence of small particulates in the $-106 + 10 \mu\text{m}$ distribution increasing their mean temperature compared to that of the $-90 + 45 \mu\text{m}$.

Figure 5 : Radial velocity (a) and surface temperature (b) distributions 75 mm downstream the nozzle exit for fused and crushed particulates with three size ranges.

Similar results are shown in figure 6 (a and b) for agglomerated particulates. For velocity, the remarks are the same as those for fused and crushed particulates. It is to be noticed that, at the measuring distance, the smallest inertia of the agglomerated particulates has already reduced the velocity difference between fused and crushed and agglomerated particulates. For surface temperatures (see figure 6.b), the lowest values are obtained with the smallest particulates. When heating agglomerated particulates, the heat propagation phenomenon is enhanced (see figure 4) especially for the big ones but the smallest particulates are heated at much higher temperatures (more than 1000 K). With the smallest particulates, which viscosity is high, the gas included in pores can escape, resulting in porous but completely molten particulates, as shown by the measurement of Bernard /19/, on the contrary with the biggest particulates the included gas blows up the molten surrounding shell, suppressing any contacts with their central core which is not heated at all, as confirmed by the SEM examinations of their cross sections. Thus, the molten shell of the bigger particulates is overheated compared to the small ones, which have also a lower residence time. This explains the higher temperature obtained with the big particulates. It is also worth to notice that the fused and crushed particulates have a shape factor in the range 0.5-0.7 and thus the size range, measured by image analysis is overestimated, the fused and crushed particulates being in fact smaller than the given size range. This induces higher surface temperatures than expected, especially for the small ones.

Figure 6 : Radial velocity (a) and surface temperature (b) distributions 75 mm downstream the nozzle exit for agglomerated particulates, with three size ranges.

When comparing fused and crushed and agglomerated particulates to agglomerated and sintered (agglomerated and sintered) ones (see fig. 8.a and b) for the - 106 + 10 μm size range, agglomerated and sintered particulates have the lowest velocity (this confirms the influence of the shape factor for the fused and crushed particulates) and of course, as already shown when comparing fig. 6 and 7, the surface temperature of the agglomerated particulates is the highest while agglomerated and sintered and fused and crushed particulates have similar surface temperature (within the experimental precision). Similar results are obtained with the - 90 + 45 μm distribution.

Figure 7 : Radial velocity (a) and surface temperature (b) distributions 75 mm downstream the nozzle exit for agglomerated, agglomerated and sintered and fused and crushed particulates in the size range $-106 + 10 \mu\text{m}$.

However for the $-45 + 10 \mu\text{m}$ distribution the velocities are in the following decreasing order : agglomerated, fused and crushed, agglomerated and sintered while the surface temperatures are successively agglomerated and sintered, fused and crushed, agglomerated. When trying to correlate these results to the Vickers hardnesses (see table 1), it can be seen first that the highest hardnesses (whatever may be the size distribution) are obtained with the fused and crushed particulates. Agglomerated particulates have lower hardnesses, especially for the $-90 + 45 \mu\text{m}$ ones at 28 kW. When the power level is raised to 40 kW the results are much better for agglomerated particulates and considering cross sections of the particulates it can be seen that the porosity is reduced. Probably this is due to the higher temperature of the particulates, inducing a lower viscosity of the molten shell and thus a better evacuation of the trapped gases. Surprisingly if the melting of the agglomerated and sintered particulates is better than that of the agglomerated ones at 29 kW (where the measurements in flight were performed) as confirmed by the hardness measurements, lower hardnesses than with agglomerated particulates are obtained with the 40 kW power level and at the moment no explanation has been found for that. However the heat treatment of the agglomerated and sintered particulates seems to be better than that of the agglomerated ones when considering table 5 where it can be seen that, except for 28 kW, no destabilization (according to the precision of the X ray measurements) occurs even after annealing at 1200°C during 72 h which is not the case of the agglomerated powders. Of course whatever may be the morphology, the best results are obtained with the $-45 + 10 \mu\text{m}$ distribution. After annealing (1200°C during 100 h) almost all the coatings have similar hardnesses. The as sprayed thermal diffusivity values follow about the same trend as that of the hardnesses except that the differences are much lower (a maximum of 20% between the lowest and the highest values).

VI - SUMMARY AND CONCLUSION

This work was devoted to a better understanding of the parameters controlling hardness of plasma sprayed zirconia coatings partially stabilized with yttria. The coatings were sprayed with a home made plasma torch with a cylindrical nozzle 8 mm in diameter and with an axial injection of the plasma gas. The plasma gas total flowrate was 90 slm with 75 slm Ar and 15 slm H_2 . The coating and substrate were cooled down during spraying with two air jets : one blown orthogonally to the plasma jet before the substrate and the other directly at the surface of the coating. A spraying distance of 8 mm was chosen as that giving the highest hardness.

Three size distributions were studied : - 45 + 10, - 90 + 45, - 106 + 10 μm as well as three different morphologies : agglomerated, agglomerated and sintered, fused and crushed powders. Two power levels were used : 29 and 40 kW, the spectroscopic study of the plasma jets showing that for currents higher than 550 A (about 43 kW) the length of the isotherms was no more increasing with the arc current due to the increased pumping of the surrounding air.

The behaviour of the particulates depends very strongly on their morphology, the best results (highest as sprayed hardness, highest resistance to destabilization) being obtained with dense particulates i.e. fused and crushed ones. For these dense particulates thermal diffusivity is also the highest but less than 20% of the lowest values. With these fused and crushed particulates the best melting is achieved of course for the - 45 + 10 μm distribution as confirmed by the surface temperature measurements, the cross section examination of the particulates after their flight in the plasma jet, the highest values of the hardness being obtained with a 40 kW power level. The surface and center temperatures calculated for 30 and 60 μm diameter particulates show that at 29 kW the first ones are completely molten down to their center while it is not the case for the 60 μm particulates. This well explains the lower hardnesses obtained with - 90 + 45 μm particulates. When using a broad distribution - 106 + 10 μm the hardness values, and thus the particulates melting are better due to the presence of the small particulates travelling in the jet fringes.

For agglomerated particulates the behaviour is quite different. The particulates smaller than 40 μm are completely molten even if the gas trapped in the pores can partly escape resulting in rather porous particulates (when collected after their flight in the plasma jet). For particulates bigger than 40 μm the trapped gas cannot escape and blows the molten external shell as a balloon resulting in uncompletely molten particulates. Of course at 28 kW the hardness of the coatings sprayed with agglomerated particulates is smaller in a ratio 1.5 compared to that obtained with fused and crushed particulates. However much better results are obtained at 40 kW, may be due to a higher temperature of the surrounding molten shell allowing the trapped gas to escape and limiting the blowing of this shell. Destabilization still occurs when annealing the coatings at 1200°C.

Agglomerated and sintered particulates which are densified result in a better melting as agglomerated particulates at 29 kW (thus hardness values intermediate between those of fused and crushed and agglomerated particulates coatings for the same size distribution). However at 40 kW they have the lowest hardness values. This shows that the heat propagation phenomenon inside porous particulates is not yet clearly understood and that measurements are still necessary to understand what happens especially for particulates flattening.

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