

Solid Particle Erosion of Plasma Sprayed Ceramic Coatings

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Thermal spraying allows the production of overlay protective coatings of a great variety of materials, almost without limitations as to its components, phases and constituents on a range of substrates. Wear and corrosion resistant coatings account for significant utilization of thermal spray processes. Besides being a means to evaluate the coating tribological performance, erosion testing allows also an assessment of the coating toughness and adhesion. Nevertheless, the relationship between the erosion behavior of thermal sprayed coatings and its microstructural features is not satisfactorily understood yet. This paper examines room temperature solid particle erosion of zirconia and alumina-based ceramic coatings, with different levels of porosity and varying microstructure and mechanical properties. The erosion tests were carried out by a stream of alumina particles with an average size of 50 μm at 70 m/s, carried by an air jet with impingement angle 90°. The results indicate that current erosion models based on hardness alone cannot account for experimental results, and, that there is a strong relationship between the erosion rate and the porosity.

Keywords: *thermal barrier, plasma spraying, erosion*

1. Introduction

Plasma sprayed coatings represents a versatile and cost-effective solution for tribological and high temperature corrosion applications. The coatings have been commercially used since 1920's. It is currently possible, by choosing the right feed stock material and coating process, as well as post-processing, to get coatings with performances comparable to conventional casting or sintered materials. A major part of thermal spray coatings – TSC - in high temperature applications lacks systematic investigation of their tribological behavior. As a consequence, users and development engineers can only count on relatively limited empirical data, that is little understood.

Solid Particle Erosion, SPE, is a wear process where particles strike against surfaces and promote material loss. During flight a particle carries momentum and kinetic energy, which can be dissipated during impact, due to its interaction with a target surface. Different models have been proposed that allow estimations of the stresses that a mov-

ing particle will impose on a target¹. The particle will also be subject to stresses and therefore it can undergo damage. However this possibility is not addressed here. It has been experimentally observed that, during the impact the target can be locally scratched² extruded³, melted⁴ and cracked² in different ways. The imposed surface damage will vary with the target material, erodent particle, impact angle, erosion time, particle velocity, temperature and atmosphere among others^{2,5}. Erosion rate, defined as the material loss per unit of erodent mass or volume, vs. impact angle, is used to distinguish the two main groups of erosion processes: ductile and brittle. During the ductile erosion process, ductile materials, like most metals at room temperature, the surface damage develops predominantly by plastic deformation. Among them include cutting, extrusion, adiabatic shear and forging. During brittle erosion process, particle impact produces different types of cracks and chipping, with negligible plastic deformation. However, on a sub-micrometer

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scale, there are evidences of plastic deformation underneath the target surface. Other evidences suggest that erosion of materials combines ductile and brittle modes simultaneously, the ratio of them depending on impact angle and material properties⁶⁻⁷.

The dynamics of a coating buildup results in a layered structure with individual lamellae oriented differently to the substrate surface, according to the spray angle^{8,9}. Pores can be seen between and inside lamellae. Brittle lamellae are frequently cracked. Gases adsorbed on the substrate surface, fluidity limitations, solidification shrinkage, phase transformation as well as gases trapped in feed stock, promote voids inside TSC. Shrinkage, thermal shock and linear expansion coefficient mismatch between substrate and coating are some of the factors responsible for coating cracking. Dimension and content of these features are determined by the spraying process parameters and feedstock material.

There is extensive literature on the relationship between mechanical properties of bulk materials and erosion rate. It has been proposed that lateral crack grow from the indentation plastic zone towards the surface originate chips. The erosion scar plastic zone produces the residual stress, which will be the driving force that determines the depth, h , and extent of lateral crack propagation. The lateral crack size being c_r , W_E , the volume loss per impact, is⁹:

$$W_E \sim (c_r^2 h) \propto (1/K^n H^m) \quad (1)$$

where n is around 4 and m around 0.25, K and H are the coating toughness and hardness.

In thermal spraying systems, for which there is no specific model has been developed, the study of erosion behavior has been mostly experimental. Variables investigated include coating thickness and surface roughness, hardness, porosity¹⁰. No general trend has been found. The present authors' analysis however observed that there are different trends for different coating systems. For example, cermets showed decreased erosion rates with increasing roughness and self-fluxing alloys showed just the opposite. In both systems hardness increased with roughness. Alumina-13Titania had the same erosion rate for average roughness values ranging from 5 to 10 μm . Erosion rates of cermet increased with porosity.

A relationship between erosion wear and coating characteristics is not always found¹¹, but in general, one expects a monotonic decrease of erosion resistance with the increase in porosity¹¹⁻¹³. However, there are conflicting data. The deleterious effect of porosity on erosion resistance has been demonstrated through tribographic features that, for example, show that the coating crashed around pores¹⁴⁻¹⁵. Pores have been found exposed¹⁶⁻¹⁷, which may affect the effective impact angle that the target sees the erodent. Kawase analyzed Ni-Cr, WC-Co and Alumina data separately and

found that, for the latter two coatings erosion resistance decreased with increase in porosity but no trend could be observed for the Ni-Cr system. There are also reports where investigators did get quantitative erosion and porosity values but they did not present any relationship between them^{18,19}. Data for WC-Ni, showed that, despite porosity increase with WC content, the erosion resistance and hardness increased for carbide contents from zero to 35 wt.% and then both hardness and erosion resistance decreased²⁰.

Porosity effects will depend also on other TSC characteristics¹¹⁻¹³. Eaton and Novak did find different correlations between porosity content and erosion rate for coatings of YSZ depending on plasma power. However, by recognizing that different pore structure may have different effects, and using an estimate for a surface area to porosity ratio they were able to find a linear correlation between erosion rate and [(internal surface area/porosity)/bending strength]¹².

Mechanical properties of coatings usually include tensile strength and hardness, which are proportional. There is still limited data on toughness. Therefore, investigators have searched for relationships between these properties and erosion resistance²¹ and linear correlation between erosion resistance and Tensile Bond Strength, Hardness and Cohesion Strength have been reported²². The two latter properties have been related to one another and their relationship with erosion resistance is reasonable since according to Eq. 1, higher hardness, or equivalent, means higher erosion resistance. Also, the relationship between hardness and porosity has been experimentally known in bulk materials²³. However, experimental results on homogeneous materials have shown that hardness alone cannot be used to indicate a general erosion trend, what is also consistent with Eq. 1. It has also been claimed that the effect of toughness in Eq. 1 is underestimated²². As to the effect of adhesion, if just a small part of the coating is removed during erosion, as mentioned before, one should not expect that adhesion would influence the wear performance. Yet, there are reports that related high adhesion with high wear performance²². Therefore, even though one may agree that erosion resistance increases with improvement of adhesion, the factors that cause it are still unclear.

In view of the opportunity to better understand the effect of porosity on erosion behavior, this paper examines incremental erosion rates at 90° impact angle and tribographic features of different classes of water stabilized plasma sprayed ceramics.

2. Experimental Procedures

Soda lime glass slide and mild carbon steel plates were tested as reference materials. Free standing parts of Alumina-3 wt.% titania (AT3), alumina-25 wt.% zirconia (AZ25), alumina-40 wt.% zirconia (AZ40) and calcia-sta-

bilized zirconia (CZ) were sprayed. The AT3 parts were produced by water stabilized plasma, using a WSP PAL 160 system (Institute of Plasma Physics Czech Republic). The AZ and CZ were sprayed with the Plasma Technik PT-2000 system, Table 1. A sample of CZ was tested in the as ground condition, which was accomplished by grinding the as sprayed samples with 600 mesh SiC grinding paper.

Room temperature SPE were carried out in a compressed air blasting type rig, under 90° impact angles, according to ASTM G76. The nozzle had a 2.2 mm ID and was kept at 15 mm stand-off distance from the target. 50 µm average size Al₂O₃ particles were used as erodent, with an average velocity of 70 m/s, as measured by a stroboscopic Control Vision® system. Weight loss was measured with 0.1 mg variability. Polished cross sections, as well as eroded surfaces of TSC, were observed under Light and Scanning Electron Microscope. The effect of SPE on the surface roughness was measured by profilometry. Porosity was determined using mercury intrusion porosimetry. The flexural strength was determined using 4-point bend testing.

3. Results and Discussion

Figure 1a shows schematically a typical incremental

erosion curve and a schematic 2D profile of an erosion scar while in Fig. 1b the measured erosion rates are plotted. Erosion rates of the reference materials, given in Table 2, fall in the ranges of previous reported values. A transient regime in the erosion process takes place, during which the incremental erosion rates decrease monotonically down to a constant steady state value. Glass however presented no transient regime. Polishing seems to reduce this transient regime.

In the tribographs of eroded WSP free standing CZ, Fig. 2, one can see intersplat boundaries and trans-splat cracked surfaces at various sites. Transgranular cracks are profuse, indicative of brittle erosion mode, and the surface of various pores are exposed. In cross section there is a fine network of cracks, even hundreds of µm away from the eroded edge, Fig. 3. The average intercrack distance in both vertical and parallel directions, relatively to the coating-substrate interface, were measured at various distances from the eroded surface of ground CZ, Table 3. It is clear that grit blasting imposes a significant increase in the density of vertical cracks.

The decrease in the wear rate with erosion time (or erodent dose) has been reported before²⁴. They postulated that, for some brittle materials, initially the target surface is thoroughly cracked with minimum material loss. Then, sig-

Table 1. Spray parameters.

Parameter	WSP	GSP (PT)
Amperage (A)	300-400	500
Voltage (V)	300-320	68
Spray Distance (mm)	350	100
Feed Distance	30	7
Feed Rate (kg/h)	33.4	2.5
Powder injection angle (°)	70	90
Injector azimuth (°)	30,150	90

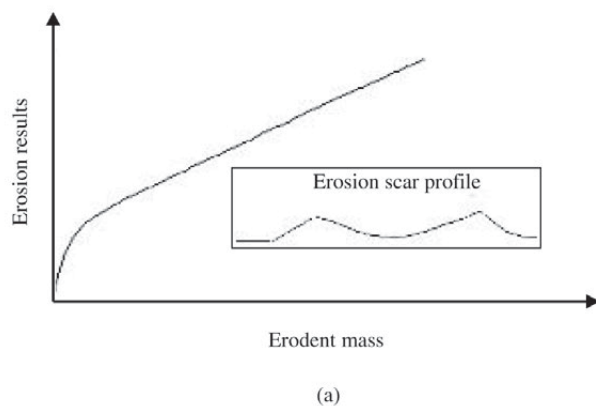


Table 2. Erosion rates of reference materials at 90° (mg/g).

Material	Average	Std. Dev
Mild Steel	0.18	0.06
Glass slide	3.2	0.1

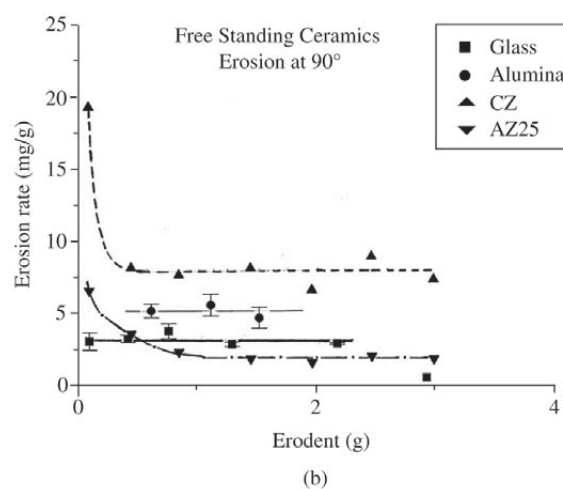


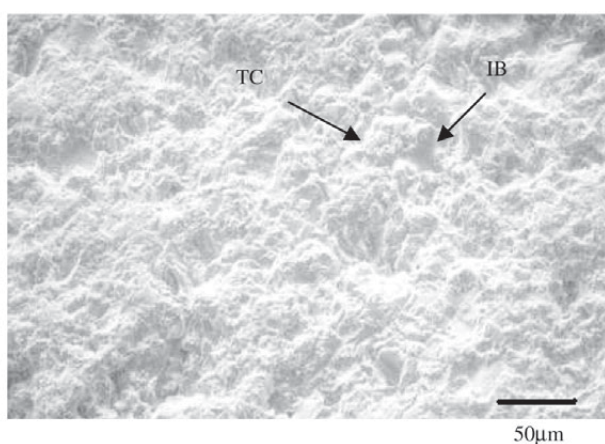
Figure 1. Erosion results. a) Schematic representation of a typical incremental erosion weight loss and 2D scar profile; b) Erosion rates of soda-lime glass, alumina, calcia-zirconia (CZ) and alumina-25 wt.% zirconia (AZ25).

Table 3. Inter-crack distance at different depths in the eroded coating of calcium stabilized zirconia (μm).

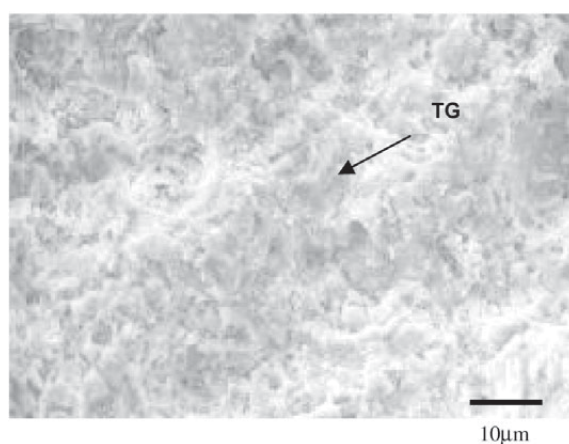
Depth μm	VERTICAL				PARALELL*			
	Ground		Eroded		Ground		As Eroded	
	Avg	Std.D.	Avg	Std.D.	Avg	Std.D.	Avg	Std.D.
0					14	7	14	5
2			2.2	0.8				
5	17	10						
10	18	2	18	4				
100	17	6	16	6	17	8	17	6

Avg = average value; Std.D. = Standard deviation.

* Measurements started at the given depth and were carried across 100 μm .



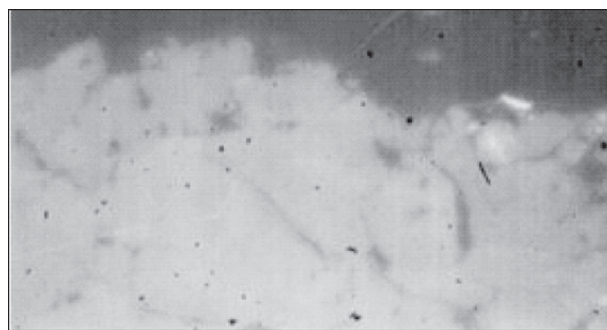
(a)



(b)

Figure 2. Tribography of CSZ sample, in eroded condition: a) 50 μm ; b) 10 μm , marks.

nificant chipping occurs, which leads to a maximum erosion rate. Further particle impact cracking proceeds, with less material removal. Later, Levy proposed that incremental erosion rate curves of brittle materials start with a high rate at the first measurable amount of erosion and that it then decreases to a much lower steady state value²⁵. This is more reasonable. The maximum values reported for reference brittle material, NiO scale, was a result of three effects interaction: NiO scale, porous NiO and Ni and therefore should not be expected to occur on single TSC. The soda-lime glass, which has a brittle behavior under the conditions used for this work, showed neither a maximum nor a monotonic decay in the incremental erosion rate. In another analysis, high surface roughness was suggested to be the responsible factor for high initial erosion rate of TSC²⁶, where protrusions are easily knocked out from as sprayed surface. Polishing TS zirconia with 1 μm alumina decreased the initial incremental erosion rate and did not alter the steady state erosion rate. Nevertheless, the material still exhibited

**Figure 3.** Cross section of a representative coating after erosion test. Cracks in the vertical (V) and parallel (P) direction are indicated.

a monotonically decreasing incremental erosion rate curve. This finding was also verified in the present work. Also, the roughness of the polished coating, which was much less

than in the as sprayed condition, significantly increased after erosion, a result also verified in this work, Table 4. The eroded surface profile changes but the average roughness does not change significantly. Considering a cross section of the as sprayed surface, there is a superposition of two waves: one with wave length on the order of 100 μm and the other with a wave length on the order of 1 to 10 μm . Most likely the high wavelength reflects the splat size and the short wavelength reflects either splashing of the liquid particles upon impact on the substrate surface or unmelted particles. These fine protusion-like coating parts are relatively loose and can be removed with less energy than what would be necessary to remove a similar part from the bulk of the coating. Consequently, during the transient erosion regime, there is a smoothed of the coating surface.

Some insight on the reasons for the SPE transient as observed in this work can come from the current modeling of brittle erosion. According to it, debris are created due to

lateral cracking and intersection between various crack types. The size of these cracks varies with load, or equivalently, impact energy. If one start a SPE experiment with a target that has a cracking structure with dimensions lower than expected for the impact energy to be used, the incremental erosion rate should increase as the cracking dimensions increase up to a steady state. If, on the other hand, the cracking dimensions and density are higher than what would be imposed by the experiment impact energy, then the erosion rate should start high and decrease to a steady state value, as the cracking dimensions and density decrease. This proposition has actually been demonstrated previously²⁷. In the case of TSC, it is possible that the near surface coating has a defect density higher than the bulk coating. With higher crack density the near surface coating toughness decreases and so does hardness, which, according to Eq. 1 should determine a higher erosion rate than the bulk coating. Also, since solid particle impact can promote significant surface heating, it is possible that crack closing happens during erosion.

The present results confirm that various tribographic features found in monolithic materials are present in TSC, more so in the high cohesion and low porosity coatings. However, significant differences exist and are related with the as sprayed surface and coating microstructure. Previous expectations that brittle thermal sprayed coatings erode by cracking and chipping mechanism, can than be just partially met²⁸. Even results for steady state erosion rates vs. impact angle for NiCrAlY at room temperature, have shown that this coating had the same erosion rate at 30 and 90^o, which denotes brittleness in the coating. Similar results found that thermal sprayed metals eroded in brittle manner³⁰.

Table 4. Average Roughness of erosion coupons (μm).

Material	As Received		Eroded to Steady State	
	Avg	Std.D.	Avg	Std.D.
Glass slide	0.013	0.005	1.5	0.1
Ground calcia-stabilized zirconia	1.3	0.3	4.5	0.4

Avg = average value

Std.D. = Standard deviation

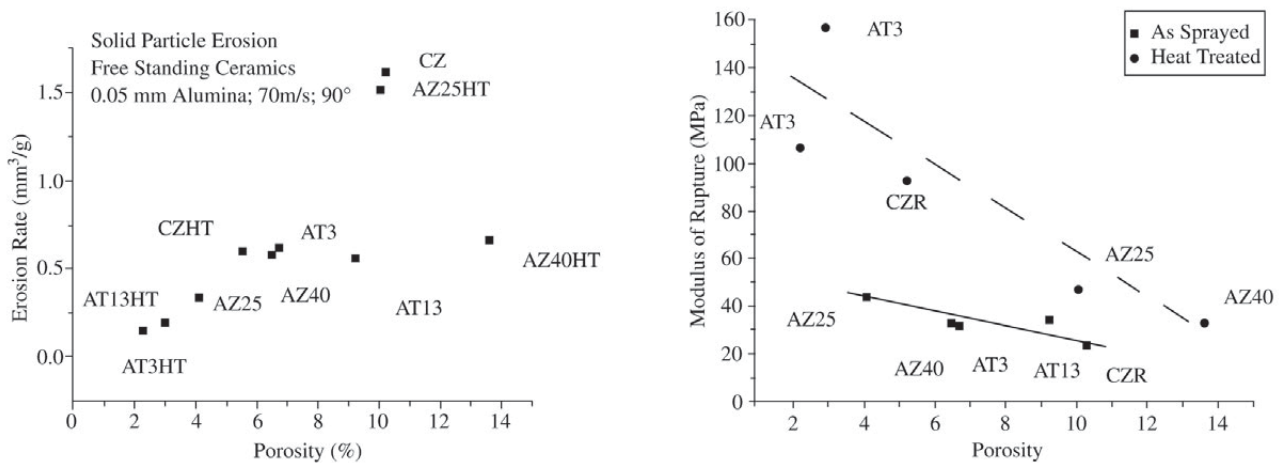


Figure 4. a) Erosion rates; b) Modulus of Rupture, as a function of porosity, of free standing parts of Alumina-3 wt. % titania (AT3) and 13wt. % titania (AT13), alumina-25 wt. % zirconia (AZ25), alumina-40 wt. % zirconia (AZ40) and calcia-stabilized zirconia (CZ), in the as sprayed and after heat treatment (HT samples).

Figure 4 shows the erosion rate and the rupture modulus as a function of porosity content. As the rupture strength decreases, one should expect that the role of intersplat decohesion should increase and the material loss per impact event should also increase, increasing the erosion rate. However, despite the fact that the coatings have very different mechanical properties at the same porosity content, it is the porosity that dictates the erosion behavior. This result shows that there must be a strong microstructural feature to be incorporated in erosion models. Porosity is definitely one very important feature, which influences erosion in three ways. Firstly, it decreases the material's strength against plastic deformation or chipping, since the material at the edge of a void lacks mechanical support. Secondly, the concave surface inside a void, that is not under the shadow of some void edge, will see an impinging particle at an angle higher than the average target surface to impact angle. This will be detrimental for brittle materials and beneficial for ductile ones. Finally, pores can act as stress concentrators and decrease the load-bearing surface.

4. Conclusion

High cohesion and low porosity coatings tend to be damaged by the same mechanisms as cast and sintered materials. The effect of porosity is significant and needs to be accounted for in erosion wear modeling. When there is high porosity content at intersplat surfaces, its effect is superimposed in the cohesion effect. Otherwise, porosity will influence erosion in three ways. Firstly, it decreases the materials strength against plastic deformation or chipping since the material at the edge of a void lacks mechanical support. Secondly, the concave surface inside a void, that is not under the shadow of some void edge, will see an impinging particle at an angle higher than the average target surface to impact angle. This will be detrimental for brittle materials and beneficial for ductile ones. Finally, pores can impair strength. They do so by acting as stress concentrators and/or decreasing the load-bearing surface.

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