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Tribological Behaviour of Alumina-Titania Nanostructured Coatings Produced by Air Plasma Spray Technique

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Nanostructured Al_2O_3-TiO_2 wear resistant coatings were produced by air plasma spray from plasma-densified agglomerated nano-powders. Conventional Al_2O_3-TiO_2 coatings were also deposited for direct comparison of tribological performance. Operating parameters were optimized by a DOE (Design of Experiment) procedure, to produce coherent and well adherent ceramic coatings and to minimize dwell times in the torch in order to reduce the risk of excessive grain growth or complete remelting. Optimal tribological behaviour was selected as the main goal function. Microstructural characterization of APS nanostructured coatings confirmed the presence of fully molten areas combined with unmolten particles still retaining their spherical morphology, and with elongated particles whose microstructure showed initial stages of grain growth and recrystallization processes. Coatings produced with the final set of deposition parameters were tested for micro-hardness, elastic modulus and unlubricated wear resistance against alumina. Results clearly indicate that nanostructured coatings produced from plasma densified nanostructured precursors exhibit considerably improved performances, evaluated in terms of worn out volume and mass loss.

1. Introduction

The development of engineering components for harsh operating conditionslike increasingly high velocity and operating contact loads, requires continuous improvement in the reliability and service life of mating surfaces, thus justifying the massive interest put in the optimization of protective coatings in the last decades. Wear resistant coatings in particular are used to reduce the damage inducedby abrasion, erosion, cavitation and fretting, which can potentially be associated with corrosion, and in some cases to reduce friction. Oxide ceramics have been widely used because of their wear resistance (as can be found in the works of Normand et al., 2000, Rainforth, 2004, and Bounazef et al., 2004) and of their protective role in the presence of thermal loads, and the fabrication processes for this kind of coatings are today well consolidated, being APS and HVOF the most efficient and economical deposition techniques.
In the very recent past many studies (from Wang et al., 2000, through Goberman et al., 2002, and Liu et al., 2004 up to the most recent Baiamonte et al, 2015, for other kinds of ceramics) focused on the possibility of depositing nanostructured oxide ceramic coatings due to potentially exceptional improvements of tribological properties (Di Girolamo et al., 2012) associated with the extremely high density of grain boundaries in these materials, provided that the nanocrystalline structure of the starting materials can be preserved during the deposition and reproduced within the coating.
In the present paper an accurate optimization of the deposition parameters of air plasma sprayed alumina-titania based coatings from commercial nanostructured powders was carried out, to reliably compare wear performance and mechanical properties of conventional and nanostructured coatings.

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2. Experimental

2.1 Precursors and coating depositions

Commercially available plasma densified clad nanostructured powders of the following composition: 73 wt% Al_2O_3 – 11 wt % TiO_2 - 9% ZrO_2 - 7% CeO_2, (Inframat, Nanox® s2613p) were deposited onto 4 mm thick aluminum plates. Small amounts of zirconia and ceria were added to the alumina-titania composition to limit grain growth during high temperature exposure (Yang et al., 2008). Coatings from conventional Al_2O_3-13%TiO_2 (METCO M130) were also deposited for direct comparison of the overall performances. Coatings were deposited by air plasma spray in a CAPS (Controlled Atmosphere Plasma Spray) thermal spray plant, using a Metco F4-MB plasma torch.

The optimal deposition parameters for nanostructured precursors were identified by a Design of Experiment (DoE) procedure. Final parameters were selected with the twofold aim of producing coherent and adherent ceramic coatings and minimizing dwell times and heat production in the torch and, consequently, the risk of excessive grain growth or complete remelting. Nine different combinations of torch parameters were tested, investigating the effect of two main factors that varied in turn at three different levels: (i) the ratio between the flow rates of secondary gases, hydrogen and helium (2/14, 9/7; 16/0), affecting thermo-kinetic properties of the flow and therefore the heat and momentum transferred to the particles in flight; (ii) the torch-to-substrate distance (between 80 and 120 mm), affecting the time of residence of the powders inside the plasma plume and the temperature of the substrate.The primary gas (argon, 41 slpm) and the total gas flow rates were kept constant for all depositions, as well as the electrical power of the torch (20.5 kW).

The influence of deposition parameters on the properties of the coatings was evaluated by examining the following characteristics: (i) average thickness of the coating, as an indirect measurement of deposition efficiency; (ii) porosity; (iii) friction coefficient (strongly affected by surface roughness in the early stages of the process); (iv) microhardness (both parallel and perpendicular to the deposition direction, due to the intrinsically non-isotropic properties of lamellar coatings); (v) elastic modulus, which is crucial for an adequate wear resistance of the coatings; (vi) weight and volume loss during tribological tests.

A goal function was defined for all coatings of the experimental matrix by selecting and assembling the sample properties and assigning a weight to each one. The input parameters selected for the optimization are resumed in Table 2, together with the measured range of values for the different coatings and the coefficient assigned for the desirability function. The parameters selected at the end of the procedure for the deposition of optimized coatings are resumed in Table 3, together with the corresponding for conventional alumina-titania powders.

Table 2: Design of experiment: input parameters for the optimization procedure and measured values

Property	Condition	Range	Units	Weight
Thickness	Maximum	378 - 455	μm	2
Porosity	Minimum	3 - 9,7	%	1
Hardness (parallel to interface)	Maximum	1071 – 1243	HK	1
Hardness (perpendicular to interface)	Maximum	977 – 1291	HK	3
Weight loss	Minimum	0,021 – 0,030	g	4
Volume loss	Minimum	2,897 – 6,224	mm^3	4
Young modulus	Maximum	153 – 283	GPa	3
Friction coefficient	Minimum	0,519 – 0,575	-	0

Table 3: Deposition parameters selected for nanostructured precursors after optimization and for conventional microstructured feedstock materials

Powder Type	**Inframat Nanox® s2613p**	**Sulzer Metco M130**	
Carrier gas (Ar)	3.5	3.5	slpm
Arc Current	600	650	A
Arc Voltage	67	70	V
Primary gas (Ar)	42	50	slpm
Secondary gas (H_2)	10	15	slpm
Secondary gas (He)	6	--	slpm
Specimen distance	90	110	mm
Number of passes	15	25	
Cooling gas (Ar)	2 nozzles at 8 bar	2 nozzles at 8 bar	

2.2 Coatings characterization

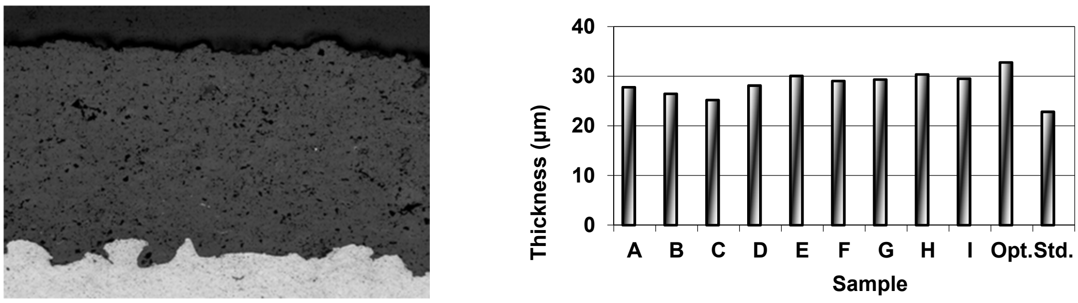
Thickness, porosity (ASTM E-2109-01) and adhesion to the substrate of the coatings were investigated and evaluated by optical microscopy (Nikon Eclipse L150) assisted by image analysis software (Leica Qwin V. 2.2

and Lucia™ 4.80). Electron microscopy analysis (Philips SEM XL40) and EDS microanalysis (Edax Falcon 106) were used to investigate and quantify the actual survival of nano- or submicro-structured phases within the coatings, evidencing growth control mechanisms and grains coalescence phenomena.
A microhardness measurement was carried out using a Knoop indenter both in parallel and perpendicularly to the interface (ASTM E-384-89). For each sample, 35 valid measurements were carried out on the two orthogonal directions, applying a load of 25 gf for 15 s.
Elastic modulus was evaluated by dynamic indentation following the Oliver and Pharr (1992) method (normal pre-load of 15 mN; loading rate of 400 mN/min; 15 s pause at the maximum load; unloading rate of 400 mN/min). For each sample 30 measurements were carried out with a load of 500 mN.
Tribological properties (wear resistance and friction coefficient) were evaluated by TE53 Slim tribometer (Plint & Partners Ltd) in the inverted block on ring configuration (Baiamonte et al., 2014) against an alumina coated aluminium disc (ASTM G77). All tests were performed at the same load (91 N), sliding velocity (1 m/s) and total distance (1 km). No third body removal system was applied. Both weight and volume loss were measured: for worn out volume evaluation a laser profilometer (Talyscan 150, Taylor-Hobson) was used with a vertical resolution of 154 nm.

3. Results and discussion

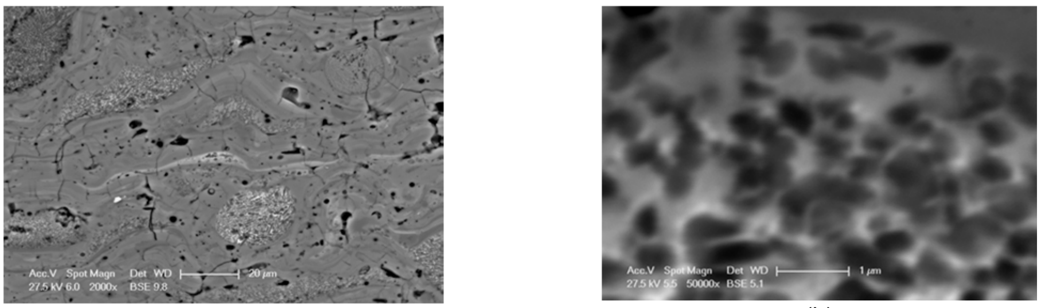
3.1 Microstructural characterization

Coatings produced from nano-structured precursors exhibit homogeneous microstructure and very high quality interfacial adhesion (Fig. 3a). Measured thicknesses of individual passes are indicated in Fig 3b. The optimization of the deposition process led to a positive gain in deposition efficiency of more than 40% as compared to conventional microstructured coatings.
The optimized deposit includes both fully molten splats and partially melted particles that were deformed to lamellar shapes without being entirely remelted (Fig.4a); inside these areas a finer microstructure can be observed, with characteristic grain size ranging from tenths to a few hundreds microns (sub-micronic structure, Fig. 4b).



(a) (b)

Figure 3: Coatings from nanostructured precursors: a, cross section of the optimized deposit (optical, 100x); b, thickness of individual passes for the nine coatings of the experimental matrix (A-I) and for the optimized (Opt) and conventional (Std) deposits



(a) (b)

Figure 4: Microstructure of the optimized coating from nanostructured precursors (SEM): a, general view of totally and partially molten splats; b, detail of sub-micronic grains

EDS maps (Fig. 5) show that the composition of the inner part of finer grains mainly consists of alumina, while the grain boundaries contain TiO_2, ZrO_2 and CeO_2. The grain boundary segregation of secondary elements is due to the effect of a Zener mechanism limiting growth and coalescence phenomena by forming a liquid, unmixable film around solid alumina particles in flight. The presence of areas of lower mechanical resistance could induce a toughening effect in the composite material.

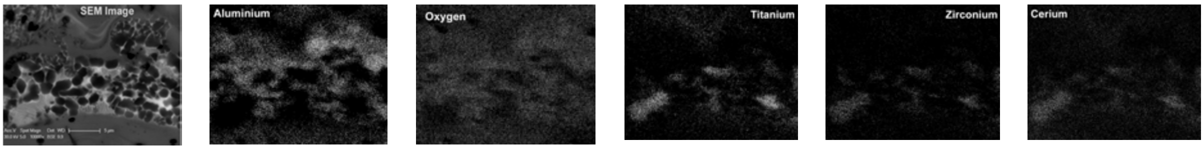


Figure 5: Detail of a nanostructured coating: EDS maps

The variation of porosity in the experimental domain is shown in Figure 6: there is a strong dependence on the plasma gas mixture composition, while spraying distance seems to affect porosity only to a limited extent. Average size and total amount of porosity for nanostructured and conventional coatings are reported in Table 4.

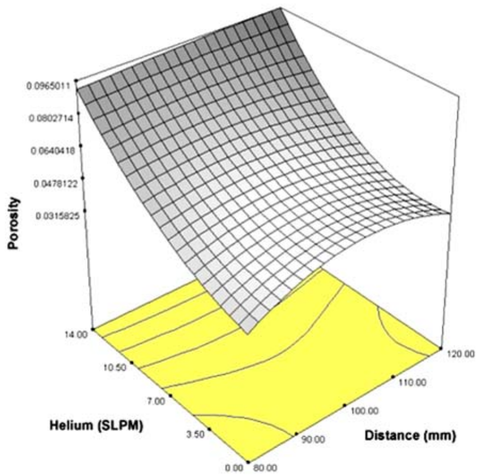


Figure. 6 Variation of porosity of nanostructured samples in the experimental domain

Table 4 Porosity (mean size and total amount) of optimized nanostructured and standard coatings

Material	Mean area of pores (μm^2)	Porosity
s2613p optimized	1,43	4,85 %
M130 (std.)	1,90	5,43 %
Variation	-24,7 %	*-10,7 %*

3.2 Microhardness and Young modulus

Variation of Knoop microhardness in the experimental domain is illustrated in Fig. 7. The values do not substantially differ in the two directions, meaning that there is a very good cohesion between lamellae. A marked increase in hardness is observed for intermediate values of plasma gas composition; this behaviour is even more evident for lower spraying distances. A comparison of hardness values for optimized nanostructured and conventional coatings is shown in Table 6. It is interesting to note that the range of variation of this parameter in the investigated domain is very wide, thus confirming the need of an accurate optimization procedure for the deposition of this kind of materials.

The variation of elastic modulus in the investigated domain is even wider (Fig. 8).

Table 5 Microhardness of optimized nanostructured and conventional coatings

Material	Knoop microhardness (parallel to interface)	Knoop microhardness (perpendicular to interface)
s2613p optimized	1214 ± 152	1235 ± 202
M130 (std.)	1054 ± 95	1073 ± 151
Variation	+15,3 %	+15,2 %

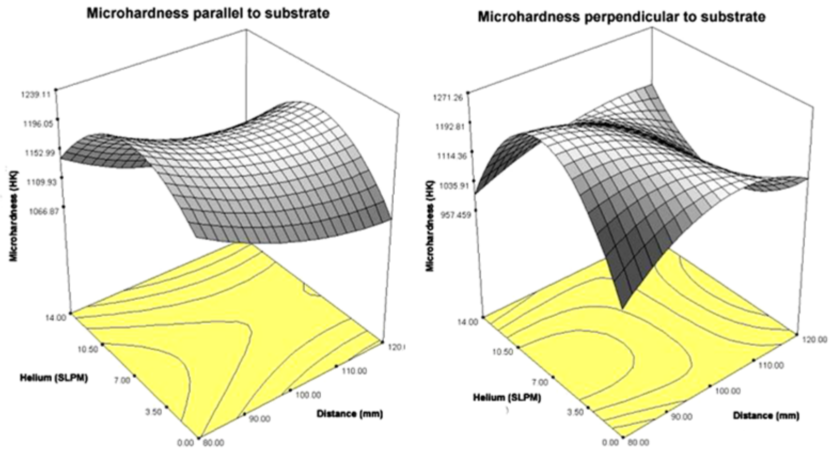


Figure. 7 Variation of microhardness (parallel and perpendicular to the substrate) of nanostructured samples in the experimental domain

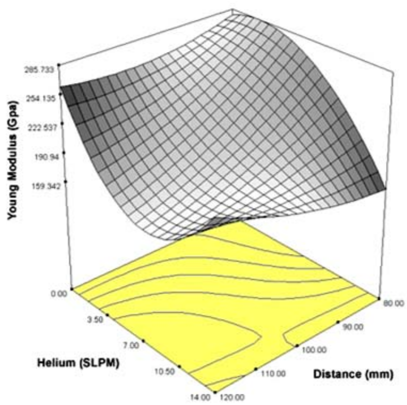
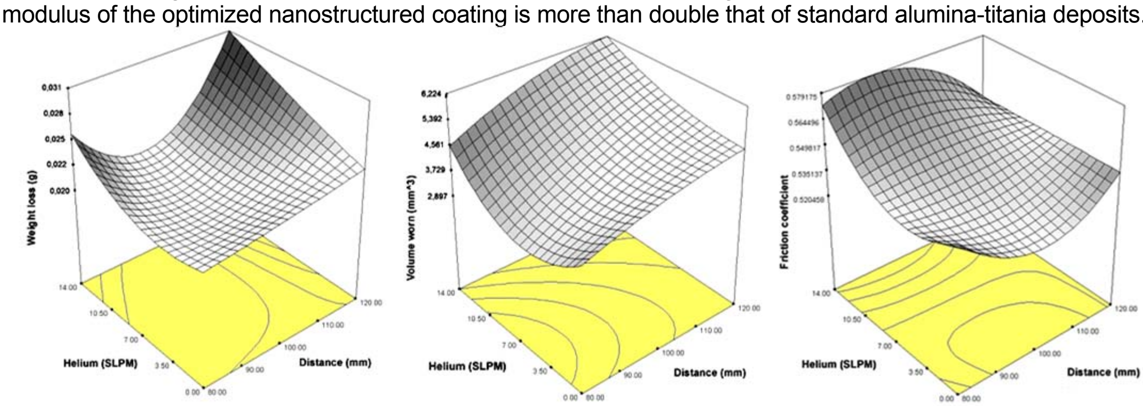


Table 6 Young modulus of optimized nanostructured and conventional coatings

Material	Test load (gf)	Young modulus (GPa)	Variation
M130 (std.)	500	151 ± 26	
s2613p optimized	250	340 ± 84	+125.2 %
s2613p optimized	500	323 ± 67	+113.9 %
s2613p optimized	1000	211 ± 29	+39.7 %

Figure 8 Variation of Young modulus of nanostructured samples in the experimental domain

In Table 6 Young modulus of conventional and nanostructured coatings is reported for different loads: the elastic modulus of the optimized nanostructured coating is more than double that of standard alumina-titania deposits.



(a) *(b)* *(c)*

Fig. 9: Variation of tribological behaviour in the experimental domain: weight loss (a), volume loss (b) and friction coefficient (c)

Table 7 Tribological response of optimized nanostructured and conventional coatings

Material	Weight loss (g)	Worn volume (mm^3)	Archard coefficient (mm^3/(N·Km))	Friction coefficient
s2613p optimized	0.025 ± 0.002	3.7 ± 0.4	0.041 ± 0.004	0.52 ± 0,07
M130 (std.)	0.035 ± 0.003	5.4 ± 0.4	0.059 ± 0.004	0.55 ± 10.03
Variation	-26.5 %	-31,5 %	-31,5 %	-5.5 %

3.3 Tribology

Wear tests results (Tab. 7, Fig. 9) show that the most important improvement in performance in terms of wear resistance is correlated to the spraying distance. Friction coefficient does not substantially vary in the experimental domain. Important improvements (about 30% for both volume and weight loss) can be observed for nanostructured coatings, as they are related to the already mentioned improvement in mechanical properties: in fact, the friction coefficient is only about 5% lower than the one shown by conventional coatings, suggesting that the wear mechanism is not likely to be altered and that the severity of the wear action is not significantly reduced.

4. Conclusions

Alumina-titania based plasma sprayed coatings obtained from nano-structured precursors are characterized by a variable amount of residual nanostructured (or sub-micron structured) ceramic grains.

The coatings outperformed conventional wear resistant ceramic deposits of similar composition. The most significant improvement was observed for tribological behaviour, with a reduction of about 30% of the wear rate. Hardness increased by about 15% and elastic modulus by up to about 110%. It is important to highlight that these results were obtained without introducing substantial modifications to the deposition process.

However, it has been demonstrated that to obtain reproducible and satisfying results, an accurate optimization procedure of the operating conditions is mandatory, since the spraying parameters affecting the degree of residual nano-structuration in the coating are numerous and they are often acting in contrast with the formation of cohesive lamellae and good quality interfaces. Moreover, the total amount of residual nano-structured phases is not the main parameter to be maximized to obtain coatings with the best wear resistance: it must instead be matched by good inter-lamellar contacts and sufficient amount of remelted grains, to guarantee the adequate overall mechanical properties of the deposit.

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