Effect of spinels on the mechanical and tribological behavior of plasma sprayed alumina based coatings

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ABSTRACT

Plasma sprayed ceramic coatings are widely used to protect metallic substrates when high temperature and/or friction are developed in service. In particular, alumina based coatings have been extensively used. Examples of applications are pistons in pumps or internal combustion engines and steam valve spindles. Alumina is hard, it shows a very high oxidation resistance and it is not permeable to aggressive gases. However, the alumina main drawback is its low fracture toughness. Brittle fracture is one of the most common wear mechanisms reported for ceramics. It is well known that the fracture toughness and the operative conditions are the key parameters controlling the crack propagation throughout the material. As a consequence, transition from mild to severe wear in ceramic coatings is mainly controlled by the fracture toughness of the coating. The typical solutions to improve the fracture behavior of alumina coatings are based on mixing alumina powders with other ceramic powders with superior toughness. Alumina – Zircona systems are used in this way.

When a mixture of ceramics is thermally sprayed, a very complex microstructure is attained in the coating. Nevertheless, a common feature can be pointed out for different systems: formation of spinels from both oxides is commonly reported. These phases seem to play an important role in the fracture behavior of the coatings and subsequently in their tribological behavior.

This paper presents a summary of the work done in the microstructural, mechanical and tribological characterization of plasma sprayed alumina based coatings (Al_2O_3 – TiO_2, Al_2O_3 – ZrO_2 and Al_2O_3 – Cr_2O_3). Special attention is paid on the role played by spinels formed during deposition.

KEY WORDS: friction, wear, ionic liquids, lubricants.

1.- INTRODUCTION

Thermal spraying technology was widely used to deposit thermal barrier coatings (TBCs). TBCs are multi-layer system consisting of a ceramic top coat, a metallic bond coat and a superalloy substrate [1]. Zirconia (ZrO_2) is one of the most employed top coats because of its high temperature resistance, chemical inertness, thermal phase stability and oxidation resistance [2].

Plasma spraying is extendedly employing to generate zirconia coatings for different applications, in example in gas turbine hot section components like burners and blades [3], because of its high production rate and low cost [2]. Thermal plasma sprayed coatings are characterized by a lamella structure and micropores, which are

good for thermal resistance and residual stress release [2]. One of the problems that may occur during plasma deposition of ceramic powder with high melting point is the high presence of interconnected pores in the coating. This could generate a loss in mechanical and chemical properties of the coating and also limits its application fields [4]. The most serious problem for a coating in a high temperature environment is the spallation generated by the thermal oxide layer that could grow at the interface. Another problem could be the loss in adhesion. This last one is closely related with wear and play an important role in determines the life of coated parts [5].
Gas tunnel-type plasma spraying was developed by A. Kobayashi [6] to produce coatings with superior properties as compared to the conventional plasma spray method [7]. With this technique, the sprayed particles can be melted efficiently and the bonding force between particles becomes stronger. The porosity is decreased and a dense coating is obtained [4]. Gas tunnel-type plasma spraying technique permits to obtain ceramic coating with a higher hardness. In example, is possible to obtain alumina coatings with a Vickers hardness of HV = 1200-1600, while an alumina sprayed coating is normally HV = 700-800 [4]. Also the adherence of the coatings was improved [5][8].
As demonstrated in several works, gas tunnel-type plasma spraying could be employed not only to generate different ceramic coatings [4][7][10][11][12], but also to produce coatings of refractory materials like tungsten [13] and Fe-base metallic glass coatings [14].
In this work, the zirconia-alumina (ZrO_2-Al_2O_3) and the alumina – chromia (Cr_2O_3 – Al_2O_3) composite coating system were studied. Previous studies permits to affirm that the combination of high hardness Al_2O_3 with the low thermal conductivity of ZrO_2 and/or Cr_2O_3, contribute to develop high functionally graded TBC with higher wear resistance [15]. In this work, mechanical and wear performance of alumina-zirconia (50/50) coatings is studied. Special attention is paid to the role played by the spinels o combined phases formed during deposition.

2.- Experimental procedure

Three sets of alumina – zircona samples (ZA1, ZA2, ZA3) were deposited using the Gas tunnel-type plasma spray technique. All of the samples were sprayed using the same starting powders (a 50/50 mixture in weight of alumina and zircona). Deposition parameters were selected to produce different amount of the spinel between alumina and zircona in the final coating. Additional samples from the alumina-chromia system (CA1 and CA2) were also deposited using a low power plasma gun. Again, deposition parameters were selected to obtain a different amount of combined phases between alumina and chromia.
The coated specimens were sectioned, mounted and grinded-polished. The microstructure of the ceramic coatings was examined using a scanning-electron microscope (SEM) Hitachi S3400N equipped with an energy dispersive X-ray (EDX) spectrometer. Compositional backscattered (BSE) and secondary electron (SE) images of the microstructure were taken.
The phase composition of the surface layers was analysed by X-ray diffraction (XRD) using a Philips PW3040/00 X'pert diffractometer with a wavelength of 1.54 Å, corresponding to Cu (Kα). Measurements were made within the 2θ angle range from 15º to 90º.

Local mechanical properties were measured using depth sensing indentation. Samples were prepared in plain view from the as-sprayed coatings. Depth-sensing indentation tests were carried out using a diamond Berkovich indenter with a nominal edge radius of 100 nm. The experimental device was a Nanoindenter XP (MTS System Co.) equipped with a high load modulus. The nanoindenter applies a load via a calibrated electromagnetic coil with a resolution of 50 nN. The displacement of the indenter was measured using a capacitive transducer with a resolution of 0.01 nm.
Scratch tests were also performed on the samples to evaluate the local wear resistance of the sample.

3.- RESULTS AND DICUSSION

Figure 1 shows SEM images from the three sets of samples deposited in the alumina – zircona system.

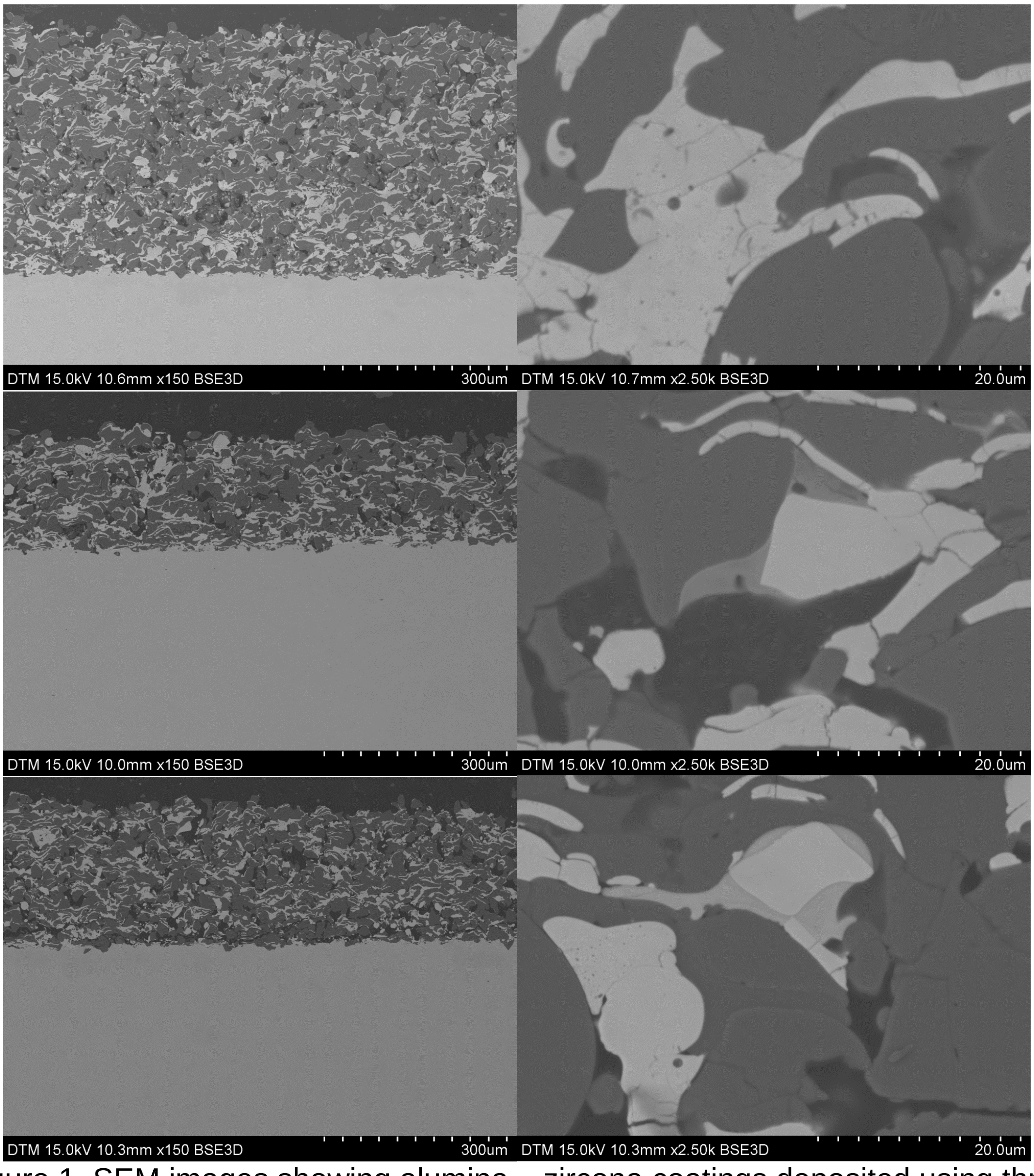

Figure 1. SEM images showing alumina – zircona coatings deposited using three different sets of deposition parameters. a) and b) AZ1. c) and d) AZ2. e) and f) AZ3.

In all samples, three different microstructural regions are detected. To clarify the composition of these zones, EDX analysis were performed in all samples. As an example, in figure 2, EDX details are showed for the ZA2 sample. However, same conclusions can be drawn or the three sets of alumina-zircona samples. The alumina – zircona coatings seem to be formed by three phases corresponding to zones 1,2 and 3 marked in figure 2. The amount of spinel in the coatings has been measured using an image analysis software. Results are collected in table 1. ZA3 sample seems to contain the larger quantity of spinel, while ZA1 appears as the coating with the lower amount of the mixed oxide. Note that as the amount of spinel increases, the coating shows a lower porosity.

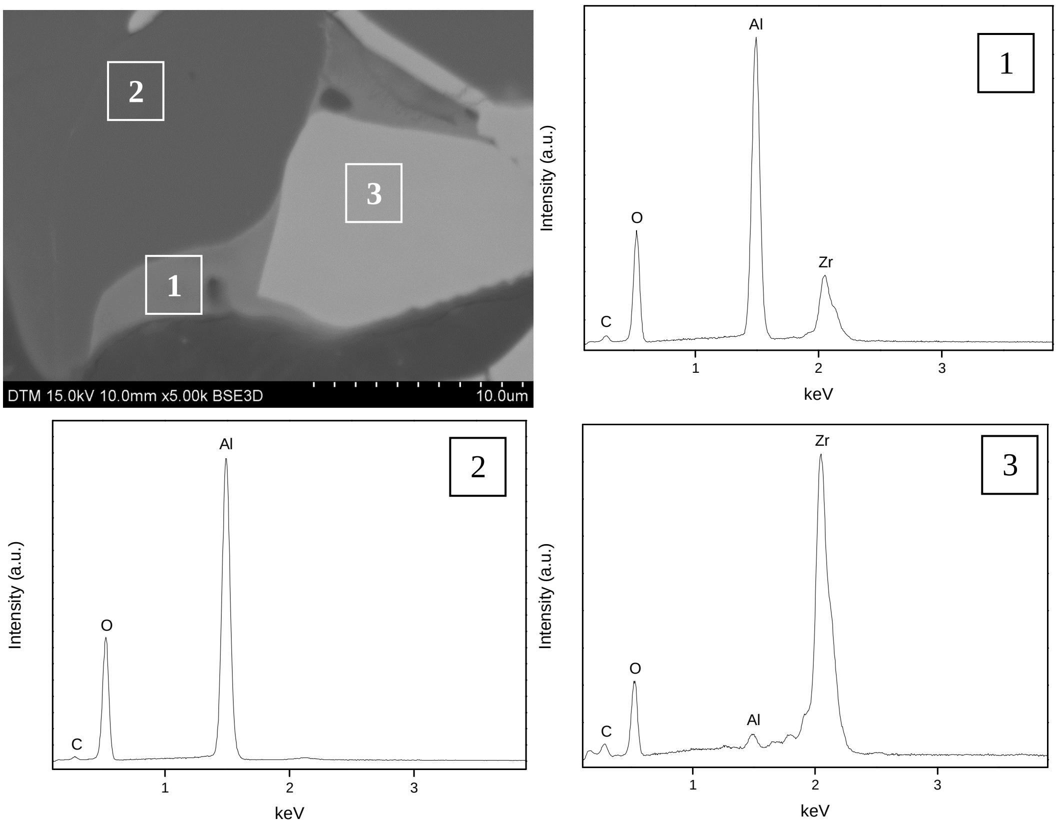

Figure 2. SEM detail of ZA2 sample showing three different microstructural regions. Zone 1 corresponds to the alumina – zircona spinel. Zone 2 is an alumina particle and zone 3 is a zircona particle.

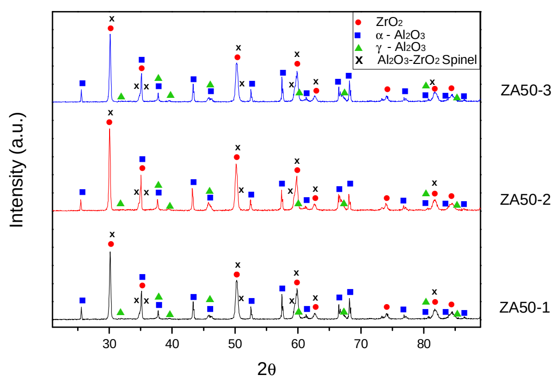

Figure 3. XRD patterns obtained from the alumina – zircona samples. In all coatings, aumin-zircona spinel is formed during deposition.

During deposition, an alumina – zircona spinel is formed by reaction of the ceramic particles. In figure 3, XRD spectra is shown for the three samples confirming the presence in the coatings of alpha and gamma alumina, cubic zircona and a mixed oxide between alumina and zircona (spinel).
Similar results can be obtained for the alumina - chromia system. Several phases can be detected in the final coating depending on the deposition parameters. In figure 4, a SEM detail of an alumina – chromia coating is showed:

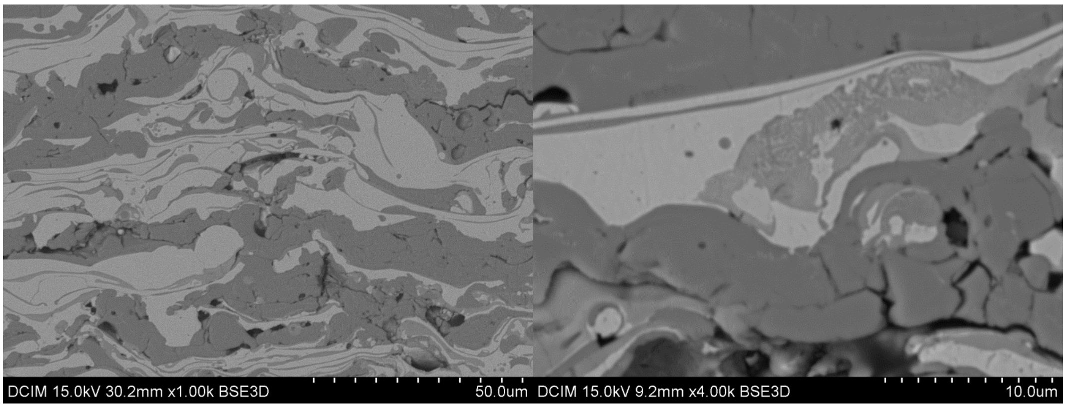

Figure 4. SEM images of an alumina – chromia system. a) Low magnification. b) High magnification.

It can be seen the presence of different microstructural regions corresponding also to a spinel formed by reaction of alumina and chromia during deposition. The question, then, is: how the amount of spinel affect the mechanical and wear behaviour of the coatings?
In table 1 Young´s modulus, hardness and fracture toughness for each phase in the coatings is measured by means of depth sensing indentation. Similar results are obtained despite the coating. The main difference is the volumetric fraction of spinel inside the coating.

Table 1: Mechanical properties and volumetric fraction measured in the coatings.

	Al_2O_3	**ZrO_2**	**Cr_2O_3**	**Spinel Alumina - Zircona**	**Spinel Alumina - Chromia**
Youngs´s Modulus (GPa)	289 ± 16	189 ± 21	134 ± 14	233 ± 18	196 ± 12
Hardness (GPa)	18 ± 3	9.5 ± 2	23 ± 2	13 ± 4	20 ± 1
Indentation Fracture toughness (MPa $m^{1/2}$)	2.8 ± 0.5	3.7 ± 0.5	3.0 ± 0.2	4.6 ± 0.6	4.8 ± 0.4
Vol. fraction ZA1 (%)*	38 ± 4	48 ± 3	-	6 ± 1	-
Vol. fraction ZA2 (%)*	32 ± 2	43 ± 2	-	11 ± 2	-
Vol. fraction ZA3 (%)*	30 ± 3	39 ± 3	-	16 ± 1	-
Vol. fraction CA1 (%)*	32 ± 3	-	47 ± 4	-	18 ± 2
Vol. fraction CA2 (%)*	43 ±5	-	45 ± 3	-	0

* Balanced for porosity

It is clear that the spinel has a superior fracture toughness than pure ceramic phases. Hardness and Young´s modulus remain between values from pure ceramics. Brittle fracture is one of the most commons wear mechanism reported for ceramic coatings. As a consequence, it is expected to obtain a higher wear resistance in the coatings that contains more amount of tough phases. As an initial approach, in figure 5, wear rate measured from scratch tests is presented for the tested coatings, confirming that the higher the amount of spinel in the coatings, the better the wear behaviour.

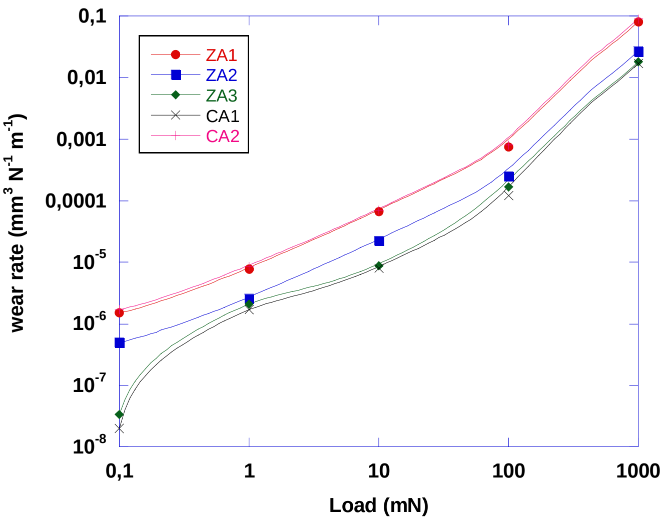

Figure 5. Wear rate versus scratch load for alumina – zirconia coating.

4.- CONCLUSIONS

In this work, microstructure, local mechanical properties and scratch behaviour of alumina based coatings deposited by plasma spray have been studied. Despite of the particular ceramic system, they present a very complex distribution of different phases comprising pure ceramic oxides and spinels formed during plasma spray of the starting powders. Spinel phase seems to be tougher than pure ceramics leading to a better wear behaviour as the amount of spinel increases in the coating.

5.- REFERENCES

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