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MECHANICAL CHARACTERISTICS OF CERAMIC COATING Al2O3 - ZRO2 DOPED OXIDE RARE EARTHS APPLIED THERMAL SPRAY FOR APPLICATION IN OIL INDUSTRY.

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Abstract. The advancement of the oil sector has generated the need for the use of materials resistant to aggressive environments to oil. Composite alumina-zirconia base reinforced with ytria oxides (rare earth), can improve the structural properties of this ceramic. This study aims to evaluate the ceramic coating Al_2O_3 - ZrO_2, sprinkled on a metal surface, using the spraying method for plasma. The coating was characterized microstructurally by SEM and evaluated for adherence assay. Ceramic coatings plasma sprayed on metal surface showed potential in structural applications in the oil sector.

Key words: alumina - zircônia, thermal spray, congress

1. Introduction

The surface degradation of used tanks in the storage and transport of oil Cru is one of the problems faced by the Oil Industry, due to the high corrosive oil power. Thus, an alternative for solving the problem is to use a kind of inert coating corrosion. Until now, ceramics based on alumina has been used where there is high demand mechanical strength and high toughness.

The fragility of the ceramic is still a factor to limit use of these materials in mechanical and industrial applications structures. To reduce the brittleness and increase the mechanical strength and toughness, ceramics are reinforced by the incorporation of one or more ceramic additives (Mainer, et al.,1994); (Sá and Morais, 2004); (Foster,et al.,2004); (Tafener,et al.,2004); (Sampaio and Tavares, 2005); (Vlack, 1997) and (Vanconcelos, 2006).

Initial studies show that the addition of small percentages of rare earth oxides in zirconia-reinforced alumina ceramics (Al_2O_3 - ZrO_2) can significantly increase the toughness of these ceramics. The process of plasma thermal spraying (APS) used for melting the coating material in powder form, the heat of a plasma arc. This process has been used in aircraft and aerospace industry, coatings for dimensional recovery, wear resistance, thermal barriers (Lima and Trevisan, 2002).

The objective of this study is to evaluate the ceramic coating Al_2O_3 - ZrO_2 + 7% Y_2O_3, sprinkled on a metal surface, using the spraying method for plasma. The coating was characterized microstructurally by SEM and evaluated for adherence assay. Ceramic coatings plasma sprayed on metallic, has been successful in structural applications in the oil sector.

2. **Materials and Methods**

Preparation of alloys

The alumina used in the spraying process was the A-1 Calcined alumina manufactured by Alcoa and adding zirconia and yttria in the composition of the ceramic alloys studied was made from commercial alloy type YSZ (yttria stabilized zirconia), Al 1075 manufactured Sulzer Metco by, composition ZrO_2 + 7% Y_2O_3. The composition of the mixtures will appear in the following table 1:

Table 1 - Composition of ceramic mixtures

composition	Mixture	Composition
Al_2O_3	80%	1
ZrO_2+7%Y_2O_3	20%	
Al_2O_3	90%	2
ZrO_2+7%Y_2O_3	10%	

The powder preparation was performed by first separation of the desired particle size range for both underwent screening process. The sieve used was of 140 mesh (106 µm.) This grain size is the same as the commercial alloy Al-1075.

The powders were weighed on precision balance and then 0.01 g were homogenized in a mechanical mixer "Y" for 50 minutes.

The material used for preparation of the bonding layer of the MCrAlY type (M = Ni, Co or NiCo) specifically alloy Ni-343 Nickel, Praxair the manufacturer, chemical composition Ni22%Cr10%Al1%Y.

Before deposition of the powders were subjected to the drying process in an a stove at 110 ° C for a period of 24 hours. This temperature ensures the dehumidification of it, which is above the water evaporation temperature and time is enough to ensure drying of the entire volume of powder in the drying trays.

The metal sheet used as substrate was kindly provided by Petrobras, and refers to a sample of the oil tank used in the company in question. It is a steel ASTM A 516 grade 60 domestic manufacturing, classified by ASTM (1987).

The surfaces of the substrates were prepared from abrasive blasting with white aluminum oxide grain 36 mesh (500 µM) with an incidence angle of 90 ° relative to the surface and approximately 150 mm apart, compressed air pressure of 60 psi as shown in the standard Petrobras in 2568 and then made the roughness measurements in portable digital roughness Mitutoyo SJ - 201.

For complete removal of impurities, dust and abrasive particles embedded in the surface it was performed an ultrasound bath for cleaning with absolute alcohol for 8 minutes.

The test sheet used for microstructural characterization, were prepared in the dimensions 100x100x5 mm.

The samples used for the adhesion test were prepared according to ASTM C633 with dimensions of 2.54 mm diameter with 30 mm length.

Planning of depositions

The deposition of coatings were implemented in partnership with the company Revesteel Metallization located in the city Pinhais in Paraná state.

Two ceramic alloys were deposited by plasma thermal spray process (APS - Atmospheric Plasma Spray), prepared from the mechanical mixture of powders of alumina-based (Al_2O_3) containing 10 and 20% yttrium stabilized zirconium (YSZ), for two preparation conditions of the substrate, with and without the presence of a bonding layer (bond coat). The bonding layer is deposited by high velocity thermal spraying process (HVOF - High Velocity Oxy-Fuel); with a nickel alloy (NiCrAlY).

For the deposition without the tie layer, or ceramic coating on the carbon steel substrate were tested three conditions of pre-heating the substrate, as follows: room temperature (RT), 150 ° C and 250 ° C.

A tensile adhesion tests (ASTM C633) alone were carried out to study the influence of the bonding layer being tested only for the alloy containing 20% of YSZ in terms of the bond coat substrate at room temperature and without bond coat with pre -heating 150 ° C. Tab. 2 summarizes the planning run depositions.

Table 2 – Planning of depositions.

Sample	Bond Coat	alloy Al_2O_3 +	Preheating
01	NiCrAlY	10%YSZ	R.T
02	NiCrAlY	20%YSZ	R.T
03	---	10%YSZ	R.T
04	---	10%YSZ	150º
05	---	10%YSZ	250º
06	---	20%YSZ	R.T
07	---	20%YSZ	150º
08	---	20%YSZ	250º
AD01	NiCrAlY	20%YSZ	R.T
AD02	---	20%YSZ	150º

- All samples were made thrice
- T. A - Ambient temperature
- AD - samples for the adhesion test

The equipment used for the application of coatings by HVOF was brand Sulzer Metco Diamond Jet gun with 2700 and the equipment used for the application of coatings by APS was brand Sulzer Metco with 9MB gun. The parameters set for these depositions were defined from the values recommended by the manufacturer for disposal of commercial aluminum alloy oxide.

The depositions were made by manual operation, and the number of passes required to achieve the desired thickness was defined by applications on test plates. The desired thickness for the bond coat was 100 to 200 µm achieved after four passes; and the ceramic layer between 200 to 300 µm reached after 15 passes.

Generally the coatings deposited by thermal spraying are produced by several passes, each pass being comprised of horizontal movements (first layer) and vertical (second layer), as shown in Figure 1.

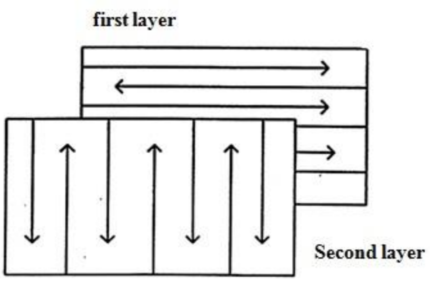
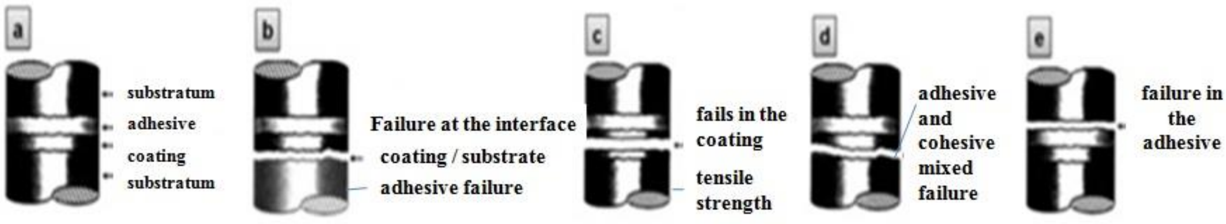


Figure 1 - Movements and layers that form a thermal spray pass (Petrobrás N 2568).

Adhesion test

A quantitative evaluation of techniques for thermally sprayed coatings is to examine the adhesion of the coatings, which meets this test, ASTM C-633, which discloses a destructive testing method for thermal spray coatings, where a test body coated is pasted to another (retest) of the same size, uncoated, and pulled with the aid of a traction machine. The evaluation is made from the voltage necessary to break the pasted samples and where hears the separation thereof. The Figure 2 below shows schematically the forms of failure that may occur in the adhesion assay.



The test piece before the test shows the assembly of Figure 2 (a); the breaking of site analysis determines the type of fault may be an adhesive when the rupture of the body occurs at the interface coating / substrate (Figure 2 (b)); cohesive that occurs between the lamellae (layers) of the coating itself (Figure 2 (c)); a mixture is mixed that the adhesive and cohesive failure (Figure 2 (d)); failure in the adhesive would be the interface with the body of evidence uncoated, indicating that the adhesion and cohesion were above the adhesive limit (Figure 2 (e)).

When premature failure occurs, or at a voltage below that expected in the adhesive region indicates that the pr e f

Figure 2 - Coating Failure modes in adherence assay. According to the standard procedure N2568 / 11.

the cohesive form is consistent say that the problem is mainly due to the process parameters or alloy problem.

The glue used for preparation of specimens for adhesion test is the Araldite Professional 24H. This adhesive requires a cure process at room temperature for 24 hours.

For the analysis of microstructure was performed SEM (scanning electron microscopy), the metallographic preparation of the deposited coatings was performed, starting with cutting the samples, followed by inlay, sanding and polishing.

Results and Discussion

Adherence

Table 3 shows the results of adhesion assay. The failure mode was the adhesive and cohesive mixed type, characteristic of ceramic coatings deposited by thermal plasma spraying.

Table 3 - Results of adhesion test.

Sample	Load (N)	Tension (MPa)	Average (MPa)
Test adhesive 1	9191	18,4	21,63
Test adhesive 2	12602	24,87	
AD 1.1	3555	7,02	7,33
AD 1.2	3326	6,56	
AD 1.3	4260	8,41	
AD 2.1	3871	7,64	8,14
AD 2.2	4176	8,24	
AD 2.3	4326	8,54	

Figure 3 is seen the AD01 experiment samples (with bond coat and without preheating) after the adhesion tests, these can be seen that failure occurred in the ceramic coating interface and the bond coat of mixed form of adhesive failure and cohesive.

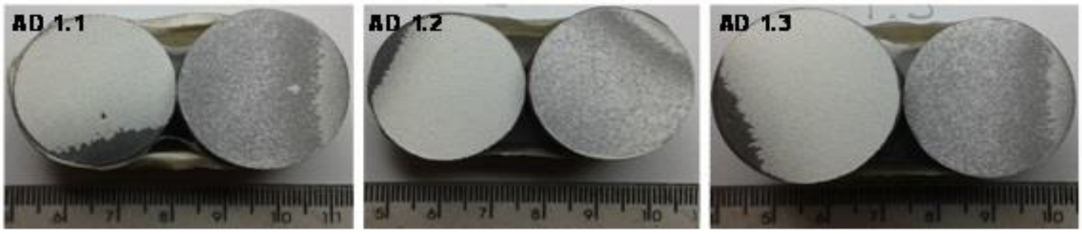


Figure 3 - AD01 experiment samples after adhesion test.

In Figure 4 is seen the AD02 experimental samples (without bond coat and preheat 150 ° C) after the adhesion test, these may be seen that the failure has also occurred in the ceramic coating interface with the substrate, a mixed manner between adhesive and cohesive failure, but with a greater exposure of the substrate, suggesting an improvement in the adhesion due to the cohesive effect of the preheating. This improvement influence the breakdown voltage values, where the results of the experiment AD02 are slightly larger than the AD01.

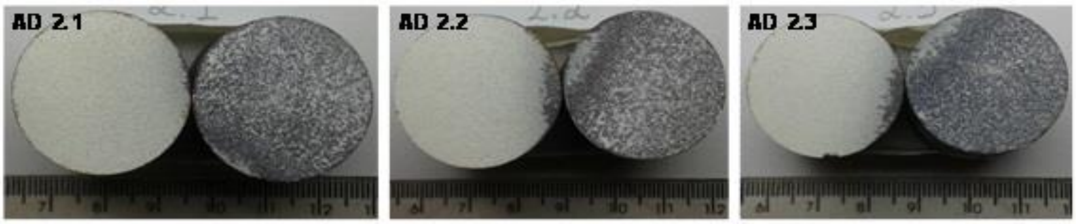
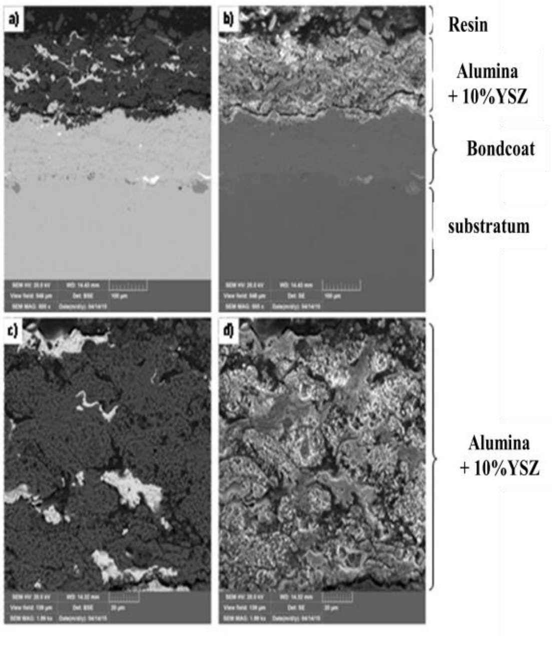
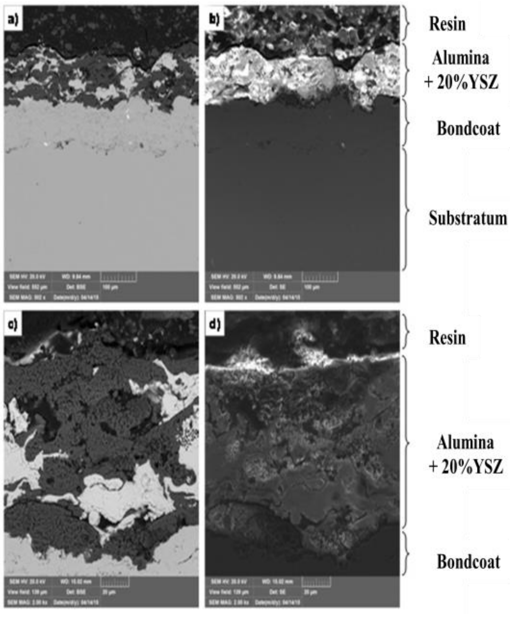


Figure 4 - AD02 experiment samples after adhesion test.

Microstructural Characterization

After blasting and measurement of roughness samples were submitted to SEM test (scanning electron microscopy) to visualize the morphology of the structure of the coatings, the figures 5 and 6 below show the micrographs:





d c) images
region by
x.

Figure 6 – experimental 02. In a) and c) images by BSE detector and b) d) the same region by the SE detector. Magnification 502 x.

ing 01 which was deposited with the alloy containing 10% YSZ on the bonding layer (bond coat). In (a) and (b) an overview of the coating is shown, where it is possible to check the distribution of the particles of YSZ, already in (c) and (d) the ceramic coating is prominent at higher magnification, showing a formed porous structure the alumina matrix. This type of morphology of the ceramic coating was observed by (Eskner, M. 2004).

The Figure 6 shows the experimental coating 02, which was deposited with the alloy containing 20% YSZ on the bonding layer (bondcoat). In (a) and (b) an overview of the coating is introduced, allowing to check the largest amount of particles of YSZ, already in (c) and (d) the ceramic coating is prominent at higher magnification, showing the same formed porous structure the alumina matrix, however it is possible to see more interaction between particles of YSZ.

Figure 7 shows the coatings of the experiments 03, 04 and 05, which was deposited with the alloy containing 10% over three YSZ substrate temperature conditions: (a) and (b) ambient temperature; in (c) and (d) pre-heating 150 ° C; and (e) and (f) pre-heating of 250 ° C. In these you can see the effect of preheating depending on pancakes YSZ, which have higher wettability due to the increase of the substrate temperature.

The effect of the wettability is characterized by more thin pancakes and elongated figure 7 (e), this occurs due to the smaller temperature gradient between the sprayed particles and the substrate, causing the particles will take longer to lose heat and solidify, it is accommodating the best surface roughness.

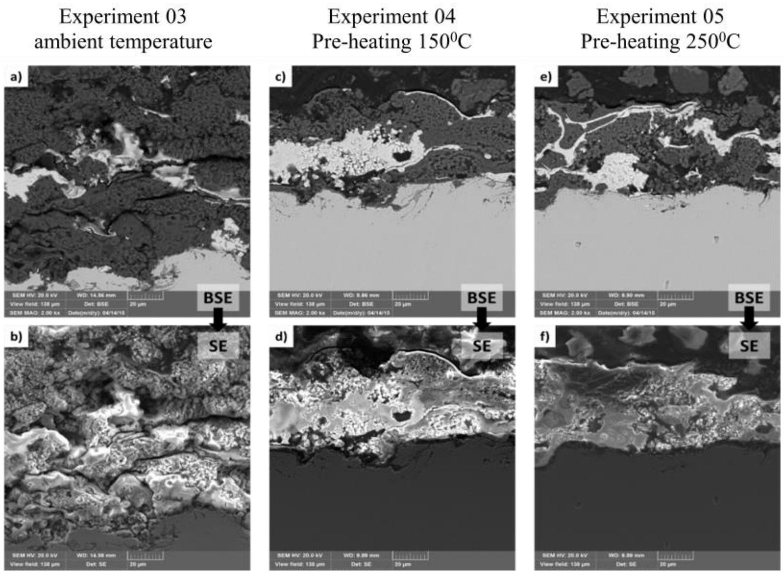


Figure 7 - Experiments deposited with alloy Al_2O_3 10% YSZ. Magnification 2.00 kx

According (HE Evans and MP Taylor, 2003) microstructure of the thermal barrier type of ceramic tiles have morphology with micro porosity with sufficient adhesion to withstand the thermal effects (swelling contraction). In the figures presented above it was observed that the deposition of the experimental alloys Al2O3 + 10% Al2O3 + YSZ and 20 YSZ% can be considered suitable for use as a thermal barrier in corrosive environments found in oil extraction.

4. Conclusions

Ceramic coatings applied by spraying plasma arc not tranfered (APS) have shown good results in industrial applications where recovery is required structures, wear resistance, among others. The spraying of ceramic samples, despite having porosity, which in turn, is inherent in the spraying process, had good adhesion and preserved the substrate, which suggests that the process can be used for metal surface protection as a thermal barrier in corrosive environments found in oil extraction.

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Mechanical Characteristics of Ceramic coating Al_2O_3 – ZrO_2 doped oxide rare earths applied thermal spray for application in oil industry.