Thermal properties of zirconia-alumina coatings obtained by thermal spray flame

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Abstract. Thermal spraying makes possible to manufacture coatings of a large number of materials, including those with a high melting point, such as ceramics. There are different ways of manufacturing these coatings, two of them are air-plasma spraying and flame spray. In this study the zirconia and alumina coatings were manufactured by flame spray, their morphology was studied and compared with their thermal conductivity and diffusivity properties. The morphology was studied from scanning electron microscope micrographs and the thermal properties measured by the laser flash method. It was discovered that the type of flame used to obtain the coatings influences the percentage porosity and thickness and that this in turn, affects its thermal properties.

1. Introduction
Thermal spraying is a technique used in the manufacture of metallic coatings, ceramics, polymers and composites. One of the main applications is as thermal barriers, useful to protect structures that work in environments of high temperature or that reach high temperature by friction. The thermal barriers coatings (TBCs), which are characterized by being thin, have a low thermal conductivity and a high resistance to thermal shock and are generally applied air-plasma spraying.

TBCs become a great success of thermal spray technology. They are made of stabilized or partially stabilized zirconia (PSZ) due to its low thermal conductivity (0.8 W/mK - 1.5 W/mK) [1], sprayed on superalloy bond coat which protects the substrate from oxidation or corrosion. However, the low thermal conductivity of zirconia greatly limits its tribological applications, because it reaches high contact temperature, when it is in friction with another material, induces thermal stresses in the coating that are detrimental to its mechanical properties. This is the reason why the alumina mixed with zirconia is used to improve the mechanical properties, since, although it has a high thermal conductivity (3 times higher than that of zirconia), it has a high hardness and is excellent for applications where wear is present. In addition, to give better structural properties to the coating, rare earth oxides such as yttria and ceria are used; they allow the zirconia to stabilize in the tetragonal and cubic phases at room temperature. For 8 wt% of yttria the structure was mainly tetragonal non-transformable and cubic and for 12 and 20 wt%, it was cubic (c) [2].
In this study, zirconia and alumina coatings were deposited in a bond coat made of a nickel-based alloy by flame spray (FS). The thermal properties were evaluated at low temperatures 323, 373, 423 and 473K, following the ASTM E 1461 [3], to determine its capacity to thermally insulate the low carbon steel pipes used in the Colombian petrochemical industry to transport heavy crude, so it is necessary to maintain the temperature of the pipes at approximately 373K, depending on their viscosity.

2. Experimental procedure

2.1. Materials and specimen preparation

Two types of commercial feedstock powders were used in the study: ZrO2-36% wt Al2O3, and alloy based on Ni of 97.62% by weight of Ni, in lesser amount, of Si, Fe, Al and Cu. Ceramic cylinders of 25.4 mm in diameter and 10 mm in thickness were used as substrates, in order to obtain two-layer coatings, without substrate. The difference of the coefficients of thermal expansion between the ceramic surface and the metallic one, generated residual tensions in the interface that did not allow the coating to adhere completely, causing its detachment.

Prior to thermal spray flame deposition, the substrates were prepared superficially with abrasive paper No. 100, followed by ultrasonic cleaning in alcohol for 15 min, obtaining a mean roughness (Ra) of 9.4 ± 3.2 μm, following the process carried out by E. Cadavid, et al. [4].

A computerized system with a Terodyn 2000 torch was employed to produce layer of coatings. The parameters of deposition for bondcoat were: an oxidant flame in the oxygen/acetylene ratio of 1:2.5, with the stand-off distance set at 15 cm and a constant powder feed rate of 46.8 g/min. The surface of the ceramic substrates at 240 °C was preheated.

Two types of oxyacetylene flame were used to obtain the ceramic coatings, one called oxidant (O) in the ratio acetylene:oxygen (1:2.5) and the other one superoxidant (SO) in the ratio (1:4.0), where the difference was the amount of oxygen supplied to the flame. When the amount of oxygen increase, the length of the hot zone increases and its temperature slightly decreases, this makes the enthalpy of the particles greater as the residence time in the flame increases and therefore the particles will melt in a greater percentage.

Three stand-off distances of 8, 9 and 10 cm were used to evaluate the influence of the residence time of the particles in the flame on the thermal conductivity of the coatings. The powder feed rate of the powder was kept constant at 9 g/min. The bondcoat was preheated to 159 °C, before depositing the ceramic layer. In total, six coatings were made with different spray conditions named: O8, O9, O10, SO8, SO9 and SO10, where the uppercase letters correspond to the flame used and the numbers to the stand-off distance.

2.2. Physical and morphological properties measurement

The coating-substrate systems were prepared metallographically in accordance with ASTM E 1920-03 [5], these were mounted in low shrinkage polymer resin and allowed to dry for 48 hours, then cut with a diamond disk at high speed, in such a way as to expose the cross-section of the coating. Then, a roughing with SiC sand paper of different grains was carried out with a sequence of P1000, P1200, P1500, P2000 and P2500, finally, it was proceeded with a polishing with a 1 μm diamond paste.

Porosity in coatings was determined via image-analysis technique using optical microscopy (OM). At least 30 optical microscopy images were taken for each coating, as specified in the standard ASTM E2109-01 [6], for this type of coatings, analyzed with the free ImageJ software.

2.3. Thermal conductivity and diffusivity measurement

The thermal conductivity and diffusivity of the two-layer coatings, the first adhesive layer (Ni-based alloy) and the ceramic top, which were removed from the substrate, were measured in an instantaneous diffusivity system (DXF200 from Netszch, Germany), equipped with a xenon lamp and an oven, according to ASTM 1461 [3]. The technique of the laser-flash method consists of subjecting the entire front surface of a small flat sample (12.5 mm in diameter) to a very short burst of energy from the xenon
lamp. An evolution of the temperature of the rear face is registered with a thermocouple or an infrared detector. From this evolution, the thermal diffusivity can be found by using the relationship [2].

\[ \kappa = 0.138785 \frac{l^2}{t_{1/2}} \]  

(1)

In the previous Equation (1), \( l \) is the tested sample thickness and \( t_{1/2} \) is the time corresponding to half of the maximum temperature of the rear face (time starts with the beginning of the flash). An analysis of the boundary conditions in this method has been made by, e.g. Pawlowski (1985) and Pawlowski et al. (1985) [2].

The working gas was nitrogen at 10 psi, the heating ramp was at a rate of 5 °C/min, for each data of three measurements were made. Diffusivity and thermal conductivity were measured in each coating at four different temperatures (323 °C, 373 °C, 423 °C and 473 °C).

Before the test, the samples were cut to the required size, using high-pressure water jet with abrasive; this technique is convenient because of its precision and because the sample does not heat up and there is no phase transformations. Finally, the samples were coated with a layer of graphite (Sprayon W204) on both sides to ensure that the sample absorbed the radiation; the face that would be in contact with the temperature sensors was coated with silver paint and the thickness of each test sample was measured. The morphology was analyzed from micrographs by scanning electron microscope (SEM).

3. Results and discussions

3.1. Physical property characterization

The physical properties of the coatings are shown in Table 1. It can be seen that the porosity depends on the type of flame, presenting a greater porosity with the SO flames, with a tendency to increase with the distance. The coating with the lowest porosity is the spraying with an oxidizing flame at a distance of 9 cm (O9). The thickest coating is also the most porous, SO8 (See Figure 1). The thinnest coatings were found for conditions SO9 and SO10, this behavior was also found by C. Cano et al. [7] who discovered that as the temperature of the flame decreases, the sample size also decreases and the amount of non-molten particles and porosity increases.

| Flame | Stand-off distance (cm) | % Porosity | Density (g cm\(^{-3}\)) | Thickness (μm) |
|-------|-------------------------|------------|-------------------------|----------------|
| O8    | 8                       | 10.41      | 5.88497821              | 659.5          |
| O9    | 9                       | 9.41       | 6.27259406              | 599.1          |
| O10   | 10                      | 10.44      | 6.28161965              | 557.7          |
| SO8   | 8                       | 10.90      | 5.91866347              | 761.6          |
| SO9   | 9                       | 10.87      | 5.92420349              | 587.1          |
| SO10  | 10                      | 10.86      | 6.15357756              | 541.2          |

Figure 1. Porosity of coatings %.
3.2. Morphology

Figure 2 and show the coatings obtained in conditions O9 (Figure 2(a)) and SO8 (Figure 2(b)) respectively, the typical characteristics of this type of coatings such as lamellas, non-molten or semi-molten particles and cracks among others are observed. Where, the areas of white, dark gray and light gray appear; the white areas correspond to the ZrO$_2$ phase, the dark gray to the Al$_2$O$_3$ phase and the light gray leaves are associated with a solid solution of ZrO$_2$ and Al$_2$O$_3$. Some researchers report similar results in coatings made with powders of the same composition, but by air-plasma spraying (APS) and using the raw material in powders and suspensions [8,9].

![Figure 2](image1.png)

(a) Figure 2. SEM micrographs showing the cross-section of the as-sprayed zirconia-alumina/ alloy based on Ni. (a) O9. (b) SO8.

3.3. Diffusivity and conductivity of coating

The thermal diffusivity for the coatings is shown in Figure 3, where the diffusivity tends to decrease with temperature, this is also found by Kakkaveri S. Ravichandran, et al. [10], for multilayer coatings by APS, which means that increasing the temperature hinders the passage of energy through the coating. The coating with the lowest thermal diffusivity is SO8, which indicates that porosity helps to improve thermal insulation.

![Figure 3](image2.png)

Figure 3. Comparison of experimental thermal diffusivity data of zirconia and alumina coatings for the four selected conditions.

![Figure 4](image3.png)

Figure 4. Comparison of experimental thermal conductivity data of zirconia and alumina coatings for the four selected conditions.
The thermal conductivity for the coatings is shown in Figure 4, these results are high, regarding to the reported conductivity of zirconia (0.8 W/mK to 1.5 W/mK), however, when comparing the results obtained for the coating of SO8 with the KS reported Ravichandran, et al. [10], it is concluded that it has a good behavior, taking into account the presence of cracks and the open porosity typical of the coatings obtained by FS [11]. If the thermal conductivity of the AISI 1020 steel 51.9 W/mK [12] is compared with that of the SO10 coating (13.98 W/mK), it is isolated 3.7 times, in the case of coating SO8 (5.95 W/mK), 8.7 times.

4. Conclusion

Effective coatings of zirconium and alumina were obtained by flame spray, to thermally insulate AISI 1020 steel substrates. The thermal properties of the coatings improve whenever they are thicker and porous; this is achieved by controlling the flame temperature and the distance of separation.

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References

[1] Fauchais P L, Heberlein J V and Boulos M I 2014 Thermal spray fundamentals (New York: Springer)
[2] Pawlowski L 2008 The science and engineering of thermal spray coatings (Washington: John Wiley & Sons)
[3] American Society for Testing and Materials (ASTM) 2007 Standard test method for thermal diffusivity of solids by the flash method Disk 6–12 mm diameter; 1.5–4 mm thick diffusivity 0.1–1,000 m2/s, ASTM E 1461 (USA: American Society for Testing and Materials)
[4] Soto-Martínez D, Parra-Velásquez C, López-Gómez M E, Vásquez-Jiménez C F and Vargas-Galvis F 2015 Copper alloy coatings manufactured by oxy-fuel thermal spray onto a porcelain substrate TecnoLógicas 18(35) 83-91
[5] American Society for Testing and Materials (ASTM) 2014 Standard guide for metallographic preparation of thermal sprayed coatings, ASTM E1920-0320 (USA: American Society for Testing and Materials)
[6] American Society for Testing and Materials (ASTM) 2014 Standard test methods for determining area percentage porosity in thermal sprayed coatings, ASTM E2109-01(USA: American Society for Testing and Materials)
[7] Cano C, Osendi M I, Belmonte M and Miranzo P 2006 Effect of the type of flame on the microstructure of CaZrO3 combustion flame sprayed coatings Surface and Coatings Technology 201(6) 3307-3313
[8] Gonzalez A G, Ageorges H, Rojas O, López E, Hurtado F M and Vargas F 2015 Efecto de la microestructura y de la microdureza sobre la resistencia al desgaste de recubrimientos elaborados por proyección térmica con plasma atmosférico a partir de circona-alumina, circona-itría y circona-ceria Boletín de la Sociedad Española de Cerámica y Vidrio 54(3) 124-132
[9] Suffner J, Sieger H, Hahn H, Dosta S, Cano I G, Guilemany J M, Klimczyk P and Jaworska L 2009 Microstructure and mechanical properties of near-eutectic ZrO2-60 wt.% Al2O3 produced by quenched plasma spraying Materials Science and Engineering A 506(1-2) 180-186
[10] Ravichandran K S, An K, Dutton R E and Semiatin S L 2004 Thermal conductivity of plasma-sprayed monolithic and multilayer coatings of alumina and yttria-stabilized zirconia Journal of the American Ceramic Society 82(3) 673-682
[11] Ferrer Pacheco M Y, Moreno Téllez C M and Vargas Galvis F Recubrimientos de circona y alúmina por proyección térmica con llama: parámetros para obtener recubrimientos de alto punto de fusión (Tunja: Universidad Pedagógica y Tecnológica de Colombia)
[12] Masanta M, Shariff S M and Roy Choudhury A 2011 A comparative study of the tribological performances of laser clad TiB2–TiC–Al2O3 composite coatings on AISI 1020 and AISI 304 substrates Wear 271(7-8) 1124-1133