

# Mechanical and tribological behavior of red clay ceramic tiles coated with fly ash powders by thermal spraying technique.

**G Peña-Rodríguez<sup>1\*</sup>, H Dulce-Moreno<sup>1</sup>, J Daza-Ramírez<sup>2</sup>, S. Orozco-Hernández<sup>2</sup> and F Vargas-Galvis<sup>3</sup>**

<sup>1</sup> Faculty of Basic Sciences. Department of Physics. GITEC group. Francisco de Paula Santander University. Cúcuta - Colombia. Av. Gran Col. # 12E-96

<sup>2</sup> Industrial Engineering. Francisco de Paula Santander University. Cucuta - Colombia.

<sup>3</sup> Pyrometallurgical and Materials Research Group (GIPIMME), University of Antioquia, Medellin Colombia.

E- mail: gabrielpr@ufps.edu.co, ggabrielp@yahoo.com

**Abstract.** The mechanical and tribological performance of red clay ceramic tiles uncoated and coated by oxy-fuel thermal spraying process from fly ash powders was evaluated. The ceramic tile substrates were manufactured by uniaxial pressing at 26.17 bar pressure, and sintered at 1100 °C. The coating thickness was determined based on the number of projection-cycles oxyacetylene flame over substrate. Coal fly ash coatings were deposited, with average thickness of 56.18±12.18 µm, 180.42±20.32 µm, and 258.26±25.88µm. The mechanical resistance to bending and wear by abrasion deep, were studied using ISO 10545-4 standards and ISO 10545-6 respectively; adhesion was measured using Elcometer equipment Type III according to ASTM D-4541-02 and the average roughness (Ra) was found according to ASTM standard D7127-13, using the profilometer Mitutoyo SJ 201. The surface morphology presented the heterogeneous molten or semi molten splats with average size of 35.262±3.48 micrometers with good adhesion, justifying increased mechanical resistance to bending by 5%, as well as wear by abrasion deep. These results contribute to the development of ceramic products with added value, to be used in various technological applications.

**Keywords:** Ceramic tiles, fly ash coatings, thermal spray, Mechanical resistance to flexion, deep abrasion wear, adherence, rugosity.

## 1. Introduction

In thermal power plants for energy production, fly ash are generated, which have applications in the construction industry and applications such as glass-ceramic materials[1-5]. Fly ash is composed mainly of mineral matter (70-80%) as glassy particles with a small proportion of crystalline phase and unburned coal. The most important minerals found in fly ash are mullite, magnetite, hematite and Silicas [5-9]. Fly ash contains amorphous spheres called cenospheres or plerospheres. Its low cost, light weight and low thermal conductivity, make them suitable for applications such as insulating blocks and as coatings for thermal protection of substrates [9-13].



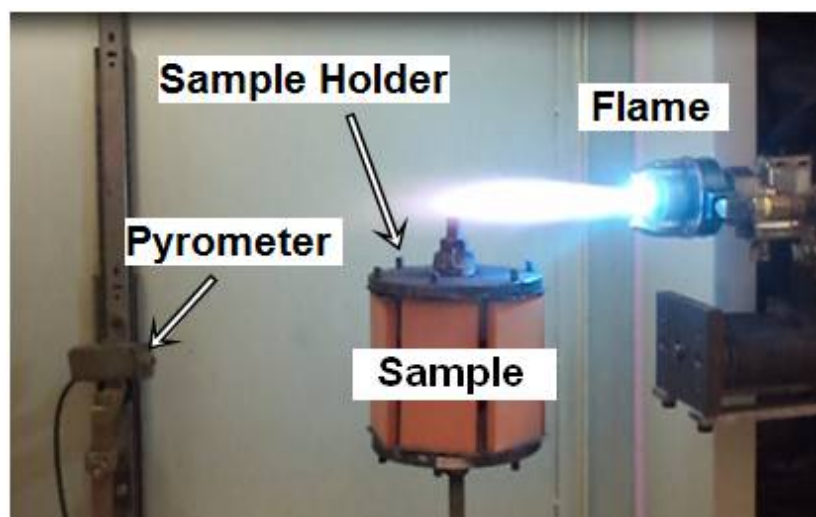
Surface treatments are considered important to improve the durability of a piece, either increasing its thermal resistance, corrosion and wear, providing material durability improving their physical appearance and their application [14]. Oxyacetylene thermal spraying (PTO) is a technique used in the recovery of worn parts, and consists of projecting small molten particles, semi-molten, hot or even cold (cold spray) which are successively deposited to a surface. The aim is to provide a surface treatment to parts which are going to be subjected to extremes of friction, wear, heat and / or mechanical stress. Choosing the coating material, the process for coating and its thickness [14], is one of the most difficult decisions for both; the manufacturer and responsible for maintenance. In addition, the PTO can cover parts of various dimensions thanks to its versatility [14-22].

Studies related to the coating of fly ash on ceramic substrates paste by the technique of PTO, were not found in the literature review of the last decade, therefore, it broke the results of studies made previously as reference studies for the determination of some working conditions, as well as previous laboratory tests.

## 2. Materials and Methods

The substrates were made from a paste of atomized red clay supplied by the company Ceramics Italia SA, (Cucuta, Colombia), with approximate dimensions of length  $L = 10$  cm, width  $A = 5$  cm, and thickness  $H = 0.8$  cm, which they were manufactured by the uniaxial pressing, using hydraulic press, with average pressure bars 26,17 ( $\approx 30,6$  Kgf /  $\text{cm}^2$ ), and humidity between 5 and 9% by weight; heat treatment (baking) was conducted using brand muffle furnace Ney D-130® with a firing curve at a maximum temperature of  $1100$  °C, with a speed of  $5$  °C / min.

For the preparation of coatings fly ash supplied by the central Termotasajero SA (Norte de Santander-Colombia) were used, which were sieved through sieve No. 270 ( $53$   $\mu\text{m}$ ) and retained mesh sieve No 325 ( $45$   $\mu\text{m}$ ) according to ASTM E-11-09.



**Figure 1.** Sample holder, pyrometer and Terodyn 2000 TM torch.  
Source: University of Antioquia group GIPIMME.

The development of the coatings was carried out using the ARESTE I chamber containing the torch Eutectic Castodin Terodyn 2000™ and sample holder hexagonal seats six (6) samples (see Fig. 1). For the screening, it was not necessary to apply anchor layer (both coat) between the substrate and projected powders, because the substrates have optimal roughness that allow adhesion of the molten particles. The projection parameters were determined by simulation using the Jets et Poudres software and pilot tests. Preheating three passes, a distance (sample-torch) of 8 cm, rotation speed of 116.0 rpm holder, vertical speed torch 0.72 cm / s, pressure and nitrogen flow of 40 psi were used and 16 L/min, respectively, while the pressure and flow of oxygen was 50 psi and 94 L/min, finally 12 psi and 22 L/min were used for the pressure and flow of acetylene, and a constant flow of powder 6 g / min.

These parameters were similar to those reported in reference [23, 24], for alumina and silica coatings. Three projections 5, 9 and 14 passes oxyacetylene flame on the substrates, values found by pilot tests and following reported by Araque et al were performed, for alumina powders on the same type of substrates [23]. The samples obtained in each projection were coded as 5P, 9P and 14P respectively.

The test for resistance to abrasion was performed according to ISO 10545-6, using the equipment Gabrielli®-CAP-3. The modulus of rupture and flexural strength was carried out according to ISO 10545-4, using equipment brand Gabrielli, Flexi-1000 LX-650 model. Adhesion test for the Pull-off type was applied, using the Elcometer Type III equipment according to ASTM D-4541-02. Microindentation hardness Vickers was performed according to standard ASTM C1327-08, which employs as diamond penetrator indenter quadrangular pyramid shaped. The average roughness (Ra) was found according to ASTM D7127-13 standard, using the profilometer Mitutoyo SJ201, for which 10 measurements and randomly oriented in different directions, with a sweep of 12.5mm was performed. The test water absorption was realized according to the UNE-EN ISO 10545-3.

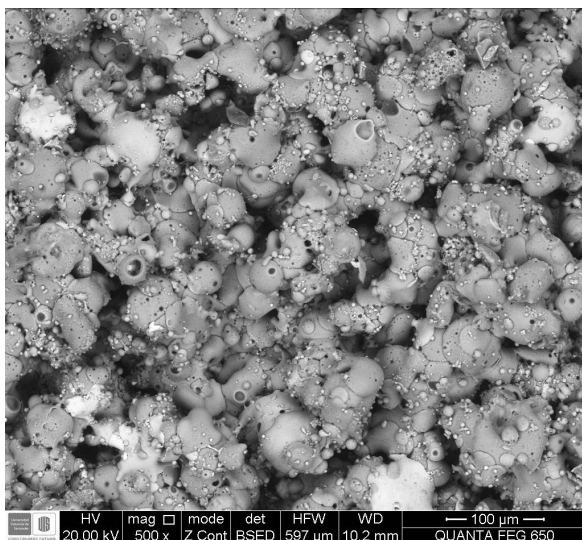
### 3. Results and discussion

Table 1 shows the Modulus of rupture by flexural, volume footprint deep abrasion, roughness and adhesion to the substrate and the three coatings 5P, 14P and 9P. It is observed that the modulus of rupture has similar behavior for the three coatings, and increases by approximately 6% compared to the modulus of rupture of the substrate. Furthermore these values comply with the technical characteristics required for wall coverings industrial level [25, 26], and are very similar to those reported by Araque et al [23], for alumina powders. It was found that as the number of passes increases the thickness increased from  $56.18 \pm 12.18 \mu\text{m}$ ,  $180.42 \pm 20.32 \mu\text{m}$  and  $258.26 \pm 25.88 \mu\text{m}$ , for 5P samples, 9P and 14P respectively, this is consistent with deep abrasion wear, because it decreases with the increasing in the number of passes, protecting the substrate up to 23.54%, since greater film thickness is better anchoring it provides to the substrate. It is also observed that the projected amount of fly ash influences the microhardness, being smaller as the number of passes or amount of fly ash increases projected. By comparing the results of the microhardness with those reported in the literature, we found that are very similar to those found in reference [24] where Vickers microhardness values are reported between  $509.85 \text{ kgf/mm}^2$  and  $713.80 \text{ kgf/mm}^2$ . On the other hand, Adhesion results are very close and range between 3.6 and 5.5 MPa, presenting cohesive failure type, showing detachment substrate and not the coating, and such values are in the range of those reported by Araque et al. [23], who reported that this parameter should be greater than 2 MPa and can be increased by heat treatment at high temperatures.

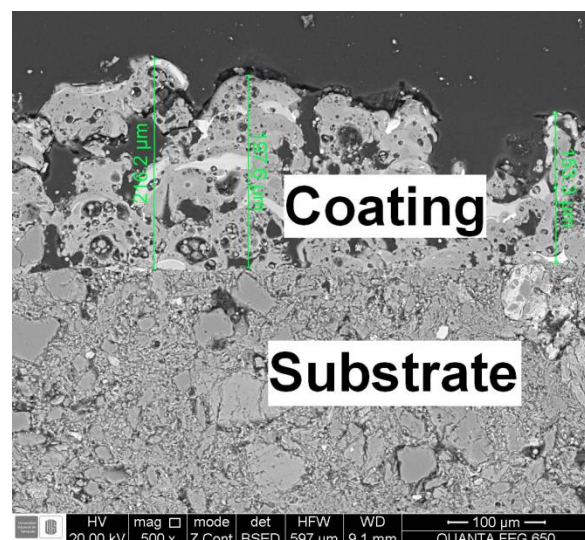
**Table 1.** Modulus of rupture by flexural, the average volume of footprint by deep abrasion, adhesion. Microhardness and roughness to the substrate and the three coatings 5P, 14P and 9P.

SAMPL E	SURFACE ROUGHNES S Ra ( $\mu\text{m}$ )	VICKERS MICROHARDNE SS (Kgf/mm <sup>2</sup> )	ADHERENC E (MPa)	DEEP ABRASION (mm <sup>3</sup> )	MODULUS OF RUPTURE (N/mm <sup>2</sup> )	WATER ABSOR PTION %
Substrat e	4.73±1.27	140.00±19.89	-	357.55±9.40	12.20±0.42	12,54
5P	15.84±0.96	616.00±95.29	4.80±0.1	128.90±2.69	12.95±0.78	12,69
9P	17.60±0.98	602.00±59.79	5.50±0.2	89.10±2.55	12.90±0.89	14,34
14P	20.44±2.41	571.00±45.3	3.60±0,3	84.15±8.69	13.05±0.92	13,77

Figure 2, shows the image of Scanning Electron Microscopy (SEM) of the surface and at Figure 3, the picture shows the SEM of a cross section for the sample 9P, to 20kV and 500X presented in these a heterogeneous morphology and molten semimolten starting powders of particles and porosities due to stacking of particles as the number of passes increases. It can be stated that as fly ash powders are deposited, its roughness is increased, protecting the substrate by deep abrasion wear, improved mechanical and tribological properties. It was found that the coating projection 2 with 9 passes, is the one with the best mechanical and tribological behavior.



**Figure 2.** SEM micrograph surface, 9P projection.



**Figure 3.** SEM micrograph cross, 9P projection.

#### 4. Conclusions

PTO technique was applied, to produce powder coatings fly ash on substrates of atomized paste prepared by uniaxial pressing, in conditions of constant thermal spraying, selected by pilot tests. The

ceramic substrate does not require any preparation because this has the characteristic of being porous, rough and chemically compatible with fly ash powders. Therefore the technique PTO on red clay substrates is viable because they allow direct anchor, getting good percentages of glassy material being the porous substrate mechanically and chemically compatible; also good results were achieved in improving the mechanical and tribological properties. Due to the homogeneity on the surface of samples no preparation was not performed. It only was made a verification that the test surface was parallel to the surface of the base or support. For the samples used, the water absorption % showed an increment of 10%, indicating that according to the UNE-EN ISO 10545-3, for tile dry pressed ceramic, are categorized within the group BIII and ISO 10545-4 according to the standard module breakage or bending strength of 12 N / mm<sup>2</sup> (equivalent to 122.40 kgf / cm<sup>2</sup>), the suggested application for covered tiles is wall covering. These results give way to future trials, which could be exploited surface porosity, it could be thinking of adding oxides to these coatings and thus provide safety features, hydrophobicity and antibacterial qualities to the samples. Finally, it is concluded that, with Projection 2 (9 passes) coating the best mechanical and tribological properties of the substrate-coating system was obtained. It is the coating having the most irregular surface topography.

### Acknowledgments

Authors are thankful to FINU-UFPS for financial support by Contract No. 026-2014, and No. 015-2015 and CODI-University of Antioquia for the financial support given to GIPIMME group through both: the PR 14-1-04 project and sustainability strategy-2014

### References

- [1] Chávez A, Vargas G, Almanza J M 2008 Caracterización y preparación de ceniza volante para su uso como recubrimientos cerámicos sobre substratos metálicos. *Bol. Soc. Esp. Ceram.* V., 47, 6, 333-8
- [2] Cheng T W and Chen Y S 2004 Characterisation of glass ceramics made from incinerator fly ash Departamento de Materiales y Recursos Minerales Ingeniería de la Universidad Nacional de Tecnología de Taipei, Taipei, Taiwán, República de China *Ceram. Int.* **30** 343–9
- [3] Ulrichs C, Schmidt U, Mucha-Pelzer T, Goswami A and Mewis I 2009 Hard Coal Fly Ash and Silica-Effect of Fine Particulate Matter Deposits on Brassica chinensis *Am. J. Agric. Bio. Sci.* **4** (1): 24-31, India
- [4] Shanthakumar S, Singh D N and Phadke R C 2008 Characterization of Fly Ash from Various Locations of Electrostatic Precipitator. The 12th *International Conference of International Association for Computer Methods and Advances in Geomechanics (IACMAG)*, October Goa, India
- [5] Arango-Martínez N, Pérez-Bueno J, Gochi-Ponce1 Y and Sánchez-Rubiol M 2011 Zeolitas a partir de cenizas volantes generadas en las centrales carboeléctricas para el tratamiento de agua contaminada con Mn y Pb. *Ciencia Ed (IMIQ)* Vol. **26** núm. 1.
- [6] Chávez-Valdez A, Arizmendi-Morquecho A, Vargas G, Almanza J M and Alvarez-Quintana J 2011 Ultra-low thermal conductivity thermal barrier coatings from recycled fly-ash cenospheres *Acta Mater.* **59** 2556–62.
- [7] Khanra S, Mallick D, Dutta S N and Chaudhuri S K 1998 Studies on the phase mineralogy and leaching characteristics of coal fly ash, *Water Air Soil Pollut* **107**:251–75
- [8] Peña-Rodríguez G and Ortega-Triana L R Morphological and structural characterization of fly ash powders 2014 *I+D* Vol. **14**, No. 2, pp. 14-19
- [9] Vucini D, Miljanovic I, Rosic A and Lazic P 2003 Effect of Na<sub>2</sub>O/SiO<sub>2</sub> mole ratio on the crystal type of zeolite synthesized from coal fly ash *J.Serb.Chem.Soc.* 68(6)471–78
- [10] Gomes S and François M 2000 Characterization of mullite in silicoaluminous fly ash by XRD, TEM and <sup>29</sup>Si MAS NMR, *Cement Concr. Res.* **30**, 175–81

- [11] Valencia S L 2001 Caracterización física química y mineralógica de las cenizas volantes Ciencia e Ingeniería Neogranadina, núm. **10**, julio, pp. 47-62, Universidad Militar Nueva Granada, Colombia
- [12] Norton G, Markuszewski R, and Shanks H 1986 Morphological and Chemical Characterization of Iron-Rich Fly Ash Fractions *Environ. Sci. Technol.* 1986, 20, 409-413 Ames Laboratory, Iowa State University, Ames, Iowa
- [13] Ruiz-Román J M, Santos C, Cambronero L, Corpas F, Alfonso M and Morano A J 2000 Aprovechamiento de las cenizas volantes, clase F, de centrales térmicas para la fabricación de materiales cerámicos. *Bol. Soc. Esp. Ceram. V.*, 39 [3] pp. 229-31
- [14] Lira-Olivares J, González-Rodulfo S, De Abreu J 2011 Recubrimientos metálicos y cerámicos solucionan el problema económico y ambiental de países desarrollados y en desarrollo *Rev. Latinam. Metal. Mat.* **31** (2): 106-121.
- [15] Morales J, Olaya-Flórez J and Rojas-Molano H 2012 An approach to thermal spray technology *AVANCES Inv. Ing.* Vol. **9** - No. 2 pp. 60-71
- [16] Chata S, Sidhu H, and Sidhu B 2012 Characterisation and corrosion-Erosion Behaviour of Carbide based Thermal Spray Coatings *J. Miner. Mater. Charact. Eng.* Vol. **11**, No. 6, pp. 569-86
- [17] Vargas F 2010 Élaboration de couches céramiques épaisses à structures micrométriques et nanométriques par projections thermiques pour des applications tribologiques Tesis de Doctorado. Faculté des sciences et techniques Université de Limoges
- [18] González A, Henao J, Díaz A, López E and Vargas F 2013 Influence of thermal spray parameters on the microstructure of Zirconia-Alumina and Zirconia-Ceria coatings used as a thermal barrier *Rev. Latinam. Metal. Mat.*, 33(2), 272-81
- [19] Cano, C 2008 “Recubrimientos cerámicos con aplicación en barreras térmicas y ambientales” Tesis doctoral Universidad Autónoma de Madrid, Madrid, España
- [20] Observatorio Tecnológico del Metal 2008 Proyección Térmica para Matrices. AIMME-Instituto Tecnológico Metalmeccánico. Parque Tecnológico
- [21] Restrepo E, Vargas F, López M, Cardona R and Duarte G 2012 Elaboración de recubrimientos cerámicos mediante proyección térmica por combustión a partir de residuos sólidos industriales *Rev. Mat.* Vol. **17**, n.4, pp. 1176-85
- [22] Pawlowski L 2008 The Science and Engineering of Thermal Spray Coatings. Second Edition Ecole Nationale Supérieure de Chimie de Lille, Villeneuve d’Ascq, France
- [23] Araque-Pabón M, Peña-Rodríguez G and Vargas-Galvis F 2015 Desempeño mecánico y tribológico de baldosas cerámicas de arcilla roja recubiertas por proyección térmica a partir de alúmina *Tecno Lógicas*, ISSN 0123-7799, Vol. 18, No. 35 pp 125-35
- [24] Vallejo-Pérez M, Gómez-García I C, Zuluaga-Castrillon D, Hernández-Ruiz J F, Vargas-Galvis F and López-Gómez M E 2013 Estudio de la estructura de recubrimientos de silicio depositados mediante proyección térmica por llama oxiacetilénica *Rev. Col. Mat.* No. **5**, pp. 145-151
- [25] <http://www.ceramicaitalia.com/inf/images/stories/WebPageFiles/FichaTecnicaRV.pdf>, consultado abril 01 de 2016
- [26] <https://alfa.com.co/uploads/fichas/99099cf35dbaf3e6c02f2ee692fa3bedb7e8c238.pdf>, consultado abril 01 de 2016