OBJECTIVES AND ANALYZING THE Al2O3-ZrO2 CERAMIC LAYERS ON METALLIC SUBSTRATE

In this case ceramic layers from Metco ZrO2 and Al2O3 powders mixture (25/75; 50/50 and 75/25) were obtained through atmospheric plasma spraying (APS) after five passes on low carbon steel substrate. The sample surfaces mechanically ground (160-2400) before and after ceramic layer deposition. Powder mixtures and the surface of ceramic thin layers were analyzed through: scanning electron microscopy (SEM). In order to understand the effect of surface wettability of the ceramic layers, before and after grinding the surface, three different liquids were used. Experimental results confirm the modification of the steel substrate surface characteristic from hydrophilic to hydrophobic when the ceramic layer was deposited. Surface free energy of hydration increases for all the samples with zirconia percentage addition before polishing process.

Keywords: ceramic layer; atmospheric plasma spraying; SEM; EDS

1. Introduction

Ceramic layers present an increasing interest in many industrial and medical applications based on their excellent properties of high hardness, corrosion (electro-corrosion) and temperature resistance [1]. Ceramic materials have, especially, in last year’s more and more applications in different fields as bulk and also as ceramic layers (thin and very thin) [2,3]. Between ceramic materials those oxides like zirconia and alumina present a special attraction based on their properties. Different methods were used to grow ceramic layers based on Al2O3 and ZrO2 like chemical vapor deposition – CVD, plasma electrolytic oxidation – PEO and atmospheric plasma spraying – APS [4-7]. Atmospheric plasma spraying (APS) represents a proper technique for ceramic layers’ deposition based on the high temperature of powders, high surface covered during deposition (robotic powder gun), industrial possibility of applications, high deposition rate and relative low price.

Contact Angle is an important parameter to measure surface wettability of solid surface. This technique implies to measure the angle formed by a liquid drop at the three-phase boundary where a liquid, gas, and solid meet. The contact angle, \( \theta \), is included between the tangent plane to the surface of the liquid and the tangent plane to the surface of the solid, at the point of intersection [8]. Low values for \( \theta \) indicate that the interaction between liquid and solid are strong and the liquid tends to spread on the solid. High \( \theta \) values indicate weak interaction and poor wetting [9]. If \( \theta \) is less than 90°, then the liquid is said to wet (or sometimes partially wet) the solid. A zero-contact angle represents complete wetting. If \( \theta \) is greater than 90°, then it is said to be non-wetting. A value 180° for \( \theta \) indicate a super non-wettable solid surface [8]. Measurement of contact angles is recommended for a better knowledge of the interactions between ceramics and liquids, which play an important role in all applications that involve a contact environment.

Many medical and industrial applications of ceramic materials use alumina and zirconia as bulk or thin films [3] and the contact with a wet environment is frequently realized. Obtaining ceramic coatings from alumina and zirconia powders (combination in different wt%) satisfy many requirements like metallic base material properties in the same time with both involved ceramic characteristic coatings. Ceramic layer roughness plays an important role in the material properties influencing the microhardness, scratch behavior and droplet contact angle.

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In this article insights about the growth of ceramic coatings through atmospheric plasma spraying using a robotic arm deposition system were given. After five passes homogeneous layers were obtained from a mixture of alumina and zirconia powders. Complex ceramic layers were analyzed before and after mechanical polish by structural point of view (SEM), roughness evolution (profilometer) and contact angle analysis.

2. Experimental details

2.1. Manufacturing of plasma spray ceramic layers

Ceramic layers were obtained from powders through APS using the parameters presented in TABLE 1. Powders were provided by Metco SC, an International producer of powders especially for Sulzer deposition gun used in this case to grow the ceramic layers. In this technique the powders reach extremely high temperatures between 12000-15000°C which melt entirely the ceramic oxides forming a homogeneity mixture [4,5].

We perform 100 determinations of the powder’s length, for Al₂O₃ and diameters for ZrO₂ powders using VegaTc software. Al₂O₃ powders have a rectangular shape, Fig. 1a), with micrometric dimensions: minimum value around 10 µm, maximum 60 µm and a mean value of 28 µm of width/length (Standard deviation was ±5 µm). Most of the ZrO₂ powders have a round shape, Fig. 1b), with an average diameter of 30 µm, a minimum size around 20 µm, a maximum value around 60 µm and an average circumference was of 100 µm. The shape of the powders used are, Fig. 1a) and b), for alumina mostly rectangular and for zirconia round.

In order to obtain layers with a proper continuity and homogeneity both shape and dimensions are important to combine two different types of powders. The mean values for both types of powders have close values (28 respectively 30 µm) encouraging the obtaining of homogeneous layers.

2.2. Surface analysis of APS ceramic layers

Ceramic particles, before and after mixture, and ceramic layers (before and after grinding) were investigated with scanning electron microscopy (SEM VegaTescan LMH II, SE detector, 30 kV electron gun power, 15.5 mm working distance

<table>
<thead>
<tr>
<th>Powder</th>
<th>9 PM powders feeder</th>
<th>Gun</th>
<th>Electric parameters</th>
<th>Ar</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carrier gas (NLPM)</td>
<td></td>
<td>DC (A)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃+ZrO₂</td>
<td>Air pressure (MPa)</td>
<td></td>
<td>DC (V)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Quantity (g/min)</td>
<td></td>
<td>P (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Distance Gun-target (mm)</td>
<td></td>
<td>Gas flow (NLPM)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>P (MPa)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Gas flow (NLPM)</td>
<td></td>
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</tr>
</tbody>
</table>

Fig. 1. SEM images of Al₂O₃ and ZrO₂ powders: Al₂O₃ in a) ZrO₂ in b), Al₂O₃+25%ZrO₂ in c), Al₂O₃+50%ZrO₂ in d) and Al₂O₃+75%ZrO₂ in e)
from ESIM-Energy Spectroscopy and Microscopy Imaging Laboratory. A problem of the layers growth through APS are the cracks and pores from the surface [10]. The appearance of these is mainly attributed to the temperature difference between the deposited and partially chiled layer the the next one at highest temperature. In order to eliminate these structural elements that influence the ceramic layer properties a mechanical grinding was realized with metalographic papers till 2000 grid. Surface profile, before and after mechanical gringing, was determined on a Taylor Hobson FORM TALYSURF 150 equipment (sensitive peak made of conical diamond, investigation distance: 30 mm, Talymap-3D Analysis Programme Package). Five experiments were performed on each sample.

2.3. Contact angle analysis

In this paper, the static contact angle of a sessile drop placed on the solid surface was measured with sessile drop technique using the device from Fig. 2.

The equipment contains a video camera equipped with a suitable magnifying lens (C), a cold light source (L.S.), a sample stage whose elevation can be controlled to high precision (M), and a syringe (S) capable to deliver a droplet with a volume about 1 μl. The drop profile was photographed, and an image analysis software (Origin Pro 2021) was used to determine the tangent of the sessile drop profile at the three-phase contact point.

The contact angle measurements were made with three test liquids, namely water, ethanol, and glycerol. Ten different regions of the sample surface were selected, taking into consideration the contact angle values of three measurements. The thermodynamic equilibrium was established by waiting for a fixed time (10 s) before recording the contact angle, except for ethanol where the drops profiles were photographed as soon as were delivered to avoid spreading and evaporation.

3. Experimental results

3.1. Morphological analyze of ceramic coatings

In Fig. 3a)-c) are highlighted the aspects of the ceramic layers deposited through APC on carbon steel substrate. Formations of molten material are present on the surface with various shapes and orientations like droplets or pie splashes. General
aspects of the surface are of non-homogeneous structural material based on different shapes of the splashes. Increasing the zirconia percentage, Fig. 3c), more round shape elements appear on the surface. At macroscopic scale the surface is cracks free and only few pores are observed on the surface. At microscopic scale the presence of cracks is observed between same and especially different shape elements (alumina and zirconia).

After mechanical grinding of the ceramic layer surfaces, Fig. 3d)-f), the surface present, in all three cases, a more homogeneous aspect, a part of the big splashes was removed and we reveal the real microstructure of the mixture alumina-zirconia that we obtained through APS. Increasing the percentage of ZrO2, Fig. 3e) and f) a finer structure can be observed. The presence of pores and micro-cracks is also identified.

The roughness of the ceramic layer’s surfaces varies consistent between initial state, Fig. 4a)-c) and mechanical grinded samples respectively Fig. 4d)-f). The main values obtained, Table 2, present the highest roughness on sample Al2O3-25%ZrO2 with Ra (arithmetic mean roughness) = 3.67 µm that can be attributed to the higher percentage of alumina and their particle irregular shape. Before grinding the sample with 75%zr2O2 present the most homogeneous surface by means of peaks and valleys presence. After grinding operation, all samples present a considerable decrease of the roughness, the smoother surface is of Al2O3-25%ZrO2 sample probably because of the software nature of alumina. All samples, with or without mechanical grinding, present deep valleys which are pores characteristic for these types of coatings.

<table>
<thead>
<tr>
<th>Sample/parameters</th>
<th>Substrate</th>
<th>P1</th>
<th>P1-p</th>
<th>P2</th>
<th>P2-p</th>
<th>P3</th>
<th>P3-p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra, µm</td>
<td>—</td>
<td>3.67</td>
<td>0.34</td>
<td>2.78</td>
<td>0.43</td>
<td>2.60</td>
<td>0.61</td>
</tr>
<tr>
<td>Rq, µm</td>
<td>—</td>
<td>3.93</td>
<td>0.46</td>
<td>3.55</td>
<td>0.58</td>
<td>3.27</td>
<td>0.96</td>
</tr>
<tr>
<td>Rsk</td>
<td>—</td>
<td>0.13</td>
<td>-1.05</td>
<td>0.03</td>
<td>-0.22</td>
<td>-0.01</td>
<td>-1.95</td>
</tr>
<tr>
<td>Rku</td>
<td>—</td>
<td>2.95</td>
<td>5.49</td>
<td>3.59</td>
<td>7.31</td>
<td>3.18</td>
<td>10.63</td>
</tr>
</tbody>
</table>
| Rq (referred to as the root-mean-square roughness) present the smaller value in first sample case, after grinding, and the biggest value for the same sample before grinding. The zirconia percentage decrease the material Rq values in case of non-grinded material and increase these values in case of grinded materials.

Mean values of main characteristics on height direction of a surface profile are Rsk and Rku (Skewness and Kurtosis). The dimension and sign of Rsk is given by the way the solid material is spread within the profile, in comparison to the median line, in our case, the material is more above the median line and then the value of the skewness parameter is negative. In one case P2 – Table 2, where the solid material is mainly below the median line then the value of the parameter Rsk is positive. Knowing that surface roughness were the heights have been removed, or with deep cracks, lead to negative values of the skewness parameter we can appreciate that the pores play an important role in determination of Rsk values in our case. After mechanical grinding

Fig. 4. Roughness profiles of samples after APS deposition: (a) Al2O3-25%ZrO2, (b) Al2O3-50%ZrO2 and (c) Al2O3-75%ZrO2
most of the peaks were removed and values of $R_{sk}$ increase also at negative part. In case of sample P2 the surface is formed by higher peaks, or smoother valleys having, before mechanical grinding a positive value of the $R_{sk}$ parameter.

Another parameter that appreciates the form of a surface is the kurtosis parameter ($R_{ku}$). If a surface is characterized by many high tips and deep valleys, holes or pores then $R_{ku} > 3$ (a leptokurtic profile) while if compared with the median line the surface present a reduced number of heights or valleys, a platykurtic profile results – $R_{ku} < 3$. Excepting sample P1 with 2.95 all the other samples present a $R_{ku}$ parameter bigger than 3 and for grinded samples even bigger than 5.7 respectively 10. $R_{z}$ (total height of surface is the vertical distance between the maximum profile peak height and the maximum profile valley depth along the evaluation length) parameter present similar values before grinding and differences after polishing based on the samples micro-hardness of the surface [11-13].

The maximum height of the profile ($R_{z} –$ indicates the absolute distance between the maximum profile peak height and the maximum profile valley depth along the profile length) presents the highest and smallest values on the same sample respectively P1 before (14.22 µm) and after (1.99 µm) mechanical grinding showing that the softer sample as surface hardness is P1. All samples in grinded state present an important reduction of $R_{z}$ values through substantial reduction of peaks during mechanical polish.

**Measurement of Static Contact Angles**

Based on Fowkes surface energy theory, which combine the Young and Young-Dupree equations [14,15], the values of the contact angles, measured with the three test liquids were used to determine the surface polarity. In this method, the surface energy has two components: a dispersive and a polar one. The dispersive component is used to evaluate the work of adhesion, expressed as, Eq. (1):

$$W_a = 2 \sqrt{\gamma_i^d \cdot \gamma_i^p} + 2 \sqrt{\gamma_i^p \cdot \gamma_i^p} = \gamma_i (1 + \cos \theta)$$  \(1\)

In this equation, $\theta$ is the contact angle of a test liquid. The indices $i$ and $s$ are states of the test liquid and the polymer solid sample, while the indices $d$ and $p$ are associated with the disperse and polar components of the surface tension.

To determine the surface tension of the solid surface, the surface tension components of the test liquids were taken from the literature [16] and Eq. (2) was applied.

$$\gamma_s = \gamma_s^d + \gamma_s^p$$  \(2\)

The surface polarity was then evaluated using Eq. (3):

$$P = \frac{\gamma_s^p}{\gamma_s^d + \gamma_s^p}$$  \(3\)

The polar and dispersive surface energy components of the tree test liquids used in this study: water (W), ethanol (E), and glycerol (G) are listed in TABLE 3.

**TABLE 3**

<table>
<thead>
<tr>
<th>Test Liquid</th>
<th>$\gamma_1$ (mJ/m²)</th>
<th>$\gamma_1^p$ (mJ/m²)</th>
<th>$\gamma_1^d$ (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (W)</td>
<td>72.8</td>
<td>51.0</td>
<td>21.8</td>
</tr>
<tr>
<td>Ethanol (E)</td>
<td>22.4</td>
<td>18.8</td>
<td>3.6</td>
</tr>
<tr>
<td>Glycerol (G)</td>
<td>64</td>
<td>30</td>
<td>34</td>
</tr>
</tbody>
</table>

To analyze the surface properties, the values of ethanol and glycerol contact angles, from TABLE 4, were introduced in Eq. (1). The values obtained are displayed in TABLE 5.

**TABLE 4**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact Angle (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percent of ZrO₂ and Al₂O₃ deposited on substrate</td>
</tr>
<tr>
<td>Before polishing process</td>
<td>P1 (ZrO₂, 25%+Al₂O₃, 75%)</td>
</tr>
<tr>
<td>P2 (ZrO₂, 50%+Al₂O₃, 50%)</td>
<td>108.61</td>
</tr>
<tr>
<td>P3 (ZrO₂, 75%+Al₂O₃, 25%)</td>
<td>113.55</td>
</tr>
<tr>
<td>After polishing process</td>
<td>P1 (ZrO₂, 25%+Al₂O₃, 75%)</td>
</tr>
<tr>
<td>P2 (ZrO₂, 50%+Al₂O₃, 50%)</td>
<td>101.75</td>
</tr>
<tr>
<td>P3 (ZrO₂, 75%+Al₂O₃, 25%)</td>
<td>102.89</td>
</tr>
<tr>
<td>Steel substrate</td>
<td>37.60</td>
</tr>
</tbody>
</table>

For all samples, obtained before and after polishing process, the dispersive component of surface tension is higher than its polar one, except for the steel substrate.

**TABLE 5**

The surface tension components of samples with different percent of ZrO₂ and Al₂O₃ deposited on steel substrate, before and after polishing process of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percent of ZrO₂ and Al₂O₃ deposited on substrate</th>
<th>$\gamma_1^p$ (mN/m)</th>
<th>$\gamma_1^d$ (mN/m)</th>
<th>$\gamma_1$ (mN/m)</th>
<th>P (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before polishing process</td>
<td>P1 (ZrO₂, 25%+Al₂O₃, 75%)</td>
<td>1.16</td>
<td>30.90</td>
<td>32.05</td>
<td>3.60</td>
</tr>
<tr>
<td>P2 (ZrO₂, 50%+Al₂O₃, 50%)</td>
<td>4.60</td>
<td>16.88</td>
<td>21.48</td>
<td>21.41</td>
<td></td>
</tr>
<tr>
<td>P3 (ZrO₂, 75%+Al₂O₃, 25%)</td>
<td>1.03</td>
<td>30.15</td>
<td>31.17</td>
<td>3.29</td>
<td></td>
</tr>
<tr>
<td>After polishing process</td>
<td>P1 (ZrO₂, 25%+Al₂O₃, 75%)</td>
<td>0.11</td>
<td>25.16</td>
<td>25.27</td>
<td>0.44</td>
</tr>
<tr>
<td>P2 (ZrO₂, 50%+Al₂O₃, 50%)</td>
<td>11.34</td>
<td>43.93</td>
<td>55.27</td>
<td>20.52</td>
<td></td>
</tr>
<tr>
<td>P3 (ZrO₂, 75%+Al₂O₃, 25%)</td>
<td>7.48</td>
<td>40.37</td>
<td>47.84</td>
<td>15.63</td>
<td></td>
</tr>
<tr>
<td>Steel substrate</td>
<td>51.92</td>
<td>3.78</td>
<td>55.71</td>
<td>93.21</td>
<td></td>
</tr>
</tbody>
</table>
Polar components increase for 25% and 50% percent of 
ZrO₂ and decrease when 75% of ZrO₂ was deposited.

The surface free energy of hydration, ΔGₜ, was estimated 
to evidence the effects of ZrO₂ deposited on the steel substrate.
The critical value for ΔGₜ is –113 mJ/m. It represents the 
equilibrium between hydrophilicity and hydrophobicity of the 
studied surface. For ΔGₜ < –113 mJ/m, the examined surface 
can be considered hydrophilic, while, when ΔGₜ > –113 mJ/m, 
it should be considered hydrophobic [17,18].

Eq. (4) [14] was used for the determination of ΔGₜ. The contact angles of water, θₜ, for the samples with different percent 
of ZrO₂ and Al₂O₃ deposited on steel substrate, before and after 
polishing process of the samples were from TABLE 2, and the 
total surface tension of water, γₜ, was 72.8 mN/m [16].

\[ \Delta G_{\text{t}} = -\gamma_{\text{t}}(1 + \cos \theta_{\text{t}}) \] (4)

The dependence of the surface free energy of hydration 
on the percent of ZrO₂ deposited on the steel substrate is 
evidenced in figure 5 for the samples before and after the polishing 
process.

From Fig. 2 it results that the steel substrate is hydrophilic 
and become hydrophobic when ceramic layer was deposited. 
Surface free energy of hydration increases for all the samples 
with addition of zirconia before polishing process. One can 
observed that ΔGₜ reached the limit between hydrophilic and 
hydrophobicity for the sample which contains 50% ZrO₂ and 
50% Al₂O₃ after the polishing process.

\[ \Delta G_{\text{t}} = -\gamma_{\text{t}}(1 + \cos \theta_{\text{t}}) \]

\[ \Delta G_{\text{t}} = -113 \text{ mJ/m} \]

Fig. 5. The dependence of the surface free energy of hydration on 
the percent of ZrO₂ deposited on the steel substrate before and after the polishing process

Conclusions

Ceramic complex coatings (alumina-(25, 50 and 75%) 
zirconia) were obtained using an atmospheric plasma spraying 
system on metallic substrate. Structural analyze performed on 
the surface of the layers present a fairly structural homogenization 
of the coatings, a high decrease of the roughness with mechani-
cal grinding and the presence of micro-cracks and pores on the 
structure.

Steel substrate surface is hydrophilic and become hydro-
phobic when ceramic layer was deposited. Surface free energy 
of hydration increases for all the coatings with addition of 
zirconia before polishing process. One can observe that surface 
free energy of hydration is situated at the boundary between 
hydrophilic and hydrophobicity for the sample which contains 
50% ZrO₂ and 50% Al₂O₃ after the polishing process.

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