THERMALLY SPRAYED COATINGS FOR HIGH TEMPERATURE APPLICATION

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Abstract

The paper deals with the relationship of the spray parameters and mechanical properties of a thermally sprayed coating on the base of ceramic materials. The main aim was directed to materials of aluminum, titanium and chromium oxides, which were sprayed using the flame spray technology (FS). Generally, ceramic coatings are standardly sprayed using the plasma spray technology (APS/VPS). APS or VPS technologies are most of all used for spraying the materials with high melting point, as the ceramic materials are, due to high operating temperature around 20 000 K. Nevertheless, several materials can be sprayed using the FS technology having in mind correct and circumspect setting of process and spray parameters. The spray parameters strongly influence the final quality of the coating and that is why it is necessary to consider them to be very significant. The amount of the fuel and oxygen in the process, spray distance and the powder feed rate are the crucial factors of the whole spray process. Amount of fuel and oxygen determine the temperature and velocity of the flame and the spray distance influence the amount of oxygen in the coatings and the coating hardness or strength. The right setting of the spray parameters is very important most of all in case of ceramic materials because of great differences between thermal expansion of a ceramic coating and a steel substrate. Bad setting of spray parameters can cause cracking inside the coating, rapid decreasing of toughness, higher porosity, higher surface roughness, lower deposition efficiency, etc. In our study ceramic coatings of Al$_2$O$_3$-3%TiO$_2$, Cr$_2$O$_3$ and TiO$_2$ were investigated. The influence of the sprayed parameters on the coating quality was investigated. The results of this study have shown that the spray distance is the most important factor for the coatings’ quality in case of ceramic materials sprayed using the FS technology. It was surprising that the flame temperature and velocity play a minor role in the optimizing process (minor influence on the coating hardness, microhardness, porosities and coating microstructure). The results of this work significantly contribute to improving knowledge about the FS sprayed ceramics and reveal some possibilities of optimizing the spraying parameters to achieve high quality coatings.

Keywords:
Flame spray, coating, spraying parameters, optimization, Al$_2$O$_3$-3%TiO$_2$, Cr$_2$O$_3$, TiO$_2$

1. INTRODUCTION

Al$_2$O$_3$-3%TiO$_2$ coating offers the resistance to the galvanic and high-temperature corrosion, the abrasive wear resistance and low coefficient of friction. Thanks to their properties they are successfully used as electrical insulators, as wear resistant coatings in the applications suffering from galvanic corrosion (pumps shafts, thermocouples). They are also applied in combustion chambers of diesel engines or in the cutting tools. Al$_2$O$_3$ powder particles are in stable α form, but after the thermal spraying they soften and transform into the γ form that decreases mechanical resistance, nevertheless increases the indentation fracture toughness of coating. The phase transformation can be a problem in flame spraying because of its lower process temperature. This ceramics material undergoes several changes in crystallographic modifications during thermal spraying due to fast cooling of coating. These transformations lead to the creating of metastable phases which decrease the indentation fracture toughness of coating. Coating toughness and hardness is influenced by the amount of TiO$_2$ addition (the influence of the addition on the tribological properties is different regarding the used thermal spray technology and powder or the powder manufacture
and its grain size). With increased amount of TiO$_2$ the hardness of whole coating decreases, its toughness increases and the porosity of coating declines. TiO$_2$ is also mainly used as the additive for improving the thermal spray process. With TiO$_2$ additive the coating adhesive strength is significantly improved. In coatings containing TiO$_2$ the following structure phases are usually detected: α-Al$_2$O$_3$, υ-Al$_2$O$_3$, Al$_2$TiO$_5$, Al$_2$Ti$_2$O$_5$ and rutile TiO$_2$. For ceramic powder spraying it is necessary to spray primarily an interlayer (bond-coat) on the substrate because between the substrate and ceramic coating high anisotropy occurs between coefficients of thermal expansivity. This anisotropy can cause excessive stresses on the boundary of the coating and substrate. Mechanical properties of coating can be improved by spraying nano-particles of the ceramic powder [1-9].

TiO$_2$ material is multifunctional having a number of potential applications such as medical technology, gas sensors and wear protection, but photocatalysis ranks among the most important ones. TiO$_2$ shows a greater photocatalytic efficiency for the degradation of organic pollutants [10]. Titania thermal spray coatings are not recommended to be used at high temperature above 540 °C due to the possibility of cracking as the result of phase transformation. It is recognized that this cracking event is based on the titania anatase-brookite to rutile phase transformation. Anatase and brookite transform irreversibly to rutile at temperatures from 400°C to 1000°C. Due to the lack of plasticity and low resilience of ceramic materials, this phase transformation tends to cause cracking and leads to failure of titania thermal spray coatings. This is a similar case to that of the Al$_2$O$_3$ coating failure caused by the υ-Al$_2$O$_3$ to α-Al$_2$O$_3$ phase transformation at high temperatures (700°C -1200°C) [11]. Microstructure of TiO$_2$ coating can be influenced by spraying parameters, mainly by the amount of the gas flow rate. Authors in [12] stated that the coating porosity and adhesive/cohesive strength can be regulated by the amount of nitrogen flow rate. Low nitrogen flow rate increases oxygen content on the splat boundaries and on the coating substrate interface.

Chromium oxide (Cr$_2$O$_3$) is an interesting material for many industrial applications due to its excellent wear and sliding properties. Poor toughness and sintering properties limits the use of Cr$_2$O$_3$ in bulk form. Limited toughness hinders also when applied as a coating. The coatings produced by different spray processes such as thermal and plasma spray techniques have various microstructure and properties. The coating structure containing in-homogeneities strongly influences its tribological behavior. In sliding of Cr$_2$O$_3$ coatings various failure mechanisms such as plastic deformation, adhesion and brittle fracture may occur. Nevertheless, thermally sprayed chromium oxide coatings have the highest wear resistance both in dry and lubricated conditions in comparison with WC-Co, Al$_2$O3 and TiO2 coatings [13, 14].

The proper choice of spraying parameters are crucial for spraying of coatings with mechanical, corrosion and high temperature properties meeting the expectation. The using of spraying parameters recommended by the powder suppliers did not lead to a coating with appropriate microstructure, properties and deposition efficiency. The experiment aimed at finding better parameters was designed and realized. Its results are described in the following paragraphs.

2. EXPERIMENT

2.1 Spraying parameters

The GTV 6P-II flame spraying equipment was used to spray all the evaluated samples. The previous grid blasting procedure, standard in VZU Plzen, was applied before spraying.

The parameters optimization procedure is based on the variation of oxygen and fuel flow. Their mutual ratio expressed by equivalent ratio $\Phi$, represents the flame temperature. The amount of gases influences the particle velocity. For some sets of parameters, the spraying distance and the amount of powder also varied. Other parameters, such as carrier gas pressure and flow, as well as travel speed and offset, remained constant. The variable parameters are summarized in Tables 1 – 3 for all tested materials.
2.2 Testing equipment
The surface hardness HR15N was measured on the as-sprayed coatings surface using the Rockwell HT 8003 hardness tester. The reported values are average ones of at least five measurements. The measured HR15N values were transferred to HRC. Then the coatings were cut, grinded and polished. The coatings microstructure was evaluated by the Nicon optical microscope using 50x, 100x and 200x magnification. The coating microhardness HV0.3 was not measured due to the difficulties with reading of indent diagonals length. The difficulties were caused by the in-homogeneity of the coatings microstructure. The abrasive wear resistance of the coatings was evaluated using the Dry Sand/Rubber Wheel test according to ASTM G 65. The reported values are the average ones of two measurements.

3. RESULTS AND DISCUSSION

Specific influence of the microstructure on the equivalent ratio (temperature of the flame) was found by means of microscopy evaluation on the coating cross sections. Nearly no powder particles melting was observed for parameters Φ < 1.3 in case of Al₂O₃+3%TiO₂ coating. These coatings were very porous and a great amount of un-melted particles occurred in the coating microstructure. These coatings were characteristic with low cohesive and adhesive strength and poor deposition efficiency. With increasing the flame temperature the particles melting was more positive, but full-melting of powder particles wasn’t achieved. A strong effect of equivalent ratio on coating microstructure was also observed at TiO₂ coatings. These coatings inclined to cracking during or after thermal spraying, which was probably caused by phase transformation, anatase and brookite transformed irreversibly to rutile. When using a colder flame, which means lower equivalent ratio, this effect was slightly suppressed. Nevertheless, some cracking was observed at all TiO₂ coatings.

3.1 Al₂O₃-3%TiO₂ coating
The results of mechanical properties evaluation of Al₂O₃-3%TiO₂ coatings, sprayed by different spraying parameters, are summarized in Fig. 1 b) and in Table 4.
As it was expected, the coating with the highest hardness showed also the highest wear resistance. If compared with Table 1 (spraying parameters), the strong influence of spraying distance can be seen. The variation of oxygen and fuel flow has only a mild effect on the hardness, and with respect to the scatter, almost no effect on the wear resistance of the Al₂O₃-3%TiO₂ coating.

**Table 4** Results of HR 15N and wear resistance according to ASTM G-65 of Al₂O₃-3%TiO₂ coating

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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<th>F</th>
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</thead>
<tbody>
<tr>
<td>Hardness HR15N</td>
<td>82.3 ± 1.9</td>
<td>61.3 ± 3.6</td>
<td>60.5 ± 3.6</td>
<td>62.6 ± 3.4</td>
<td>62.5 ± 7.2</td>
<td>64.8 ± 7.9</td>
</tr>
<tr>
<td>Wear rate [10⁻⁵ g/m]</td>
<td>83 ± 3.8</td>
<td>138 ± 5.4</td>
<td>156 ± 12.8</td>
<td>121 ± 1.3</td>
<td>157 ± 10.9</td>
<td>151 ± 21.3</td>
</tr>
</tbody>
</table>

![Microstructure of Al₂O₃-3%TiO₂ coating, sprayed by GTV P-II](image1)

![Cumulative mass loss vs. abrasive distance](image2)

**Fig. 1** Microstructure of Al₂O₃-3%TiO₂ coating, sprayed by GTV P-II (a) and ASTM G-65 results (b)

### 3.2 Cr₂O₃ coating

The results of mechanical properties evaluation of Cr₂O₃ coatings, sprayed by different spraying parameters, are summarized in Fig. 2 b) and in Table 5.

![Microstructure of Cr₂O₃ coating, sprayed by GTV P-II](image3)

![Cumulative mass loss vs. abrasive distance](image4)

**Fig. 2** Microstructure of Cr₂O₃ coating, sprayed by GTV P-II a) and ASTM G-65 results (b)
Table 5 Results of HR 15N and wear resistance according to ASTM G-65 of Cr$_3$O$_2$ coating

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
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<th>D</th>
<th>E</th>
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<tbody>
<tr>
<td>Hardness HR15N</td>
<td>77.3 ± 2.4</td>
<td>73.3 ± 3.6</td>
<td>74.0 ± 7.4</td>
<td><strong>81.8 ± 5.6</strong></td>
<td>79.3 ± 4.7</td>
<td>78.3 ± 5.5</td>
<td>80.1 ± 1.8</td>
</tr>
<tr>
<td>Wear rate [10$^5$ g/m]</td>
<td>134 ± 8.6</td>
<td>172 ± 58.2</td>
<td><strong>57 ± 18</strong></td>
<td>140 ± 3.7</td>
<td>84 ± 26.9</td>
<td>64 ± 37.0</td>
<td>80 ± 0.12</td>
</tr>
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</table>

In the case of Cr$_2$O$_3$ coating, the variation between the measured values of surface hardness HR15N is very low. On the contrary, the differences between wear rates are high (compare results of F and A coatings with comparable surface hardness and double wear rate). Even if for abrasion wear the microhardness is more relevant parameter than the surface hardness, such a discrepancy is bigger than acceptable. The reason can be found in the poor coating microstructure. The low intersplat cohesion causes high wear rate in the abrasive conditions.

Also in the case of Cr$_2$O$_3$ coating, no measurable influence of equivalent ration on the evaluated properties was observed.

3.3 TiO$_2$ coating

The results of mechanical properties evaluation of TiO$_2$ coatings, sprayed by different spraying parameters, are summarized in Fig. 3 b) and in Table 6. For TiO$_2$ coating, the results of surface hardness and wear resistance are in a good agreement. Also for TiO$_2$ coating, the only significant effect was recorded in the case of variation of the spraying distance.

![Fig. 3 Microstructure of TiO$_2$ coating, sprayed by GTV P-II a) and ASTM G-65 results (b) (a)](image)

![Fig. 3 Microstructure of TiO$_2$ coating, sprayed by GTV P-II a) and ASTM G-65 results (b) (b)](image)

Table 6 Results of HR 15N and wear resistance according to ASTM G-65 of TiO$_2$ coating

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
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<tbody>
<tr>
<td>Hardness HR15N</td>
<td>49.0 ± 27.5</td>
<td><strong>82.1 ± 3.1</strong></td>
<td>77.1 ± 4.5</td>
<td>76.7 ± 6.6</td>
<td>71.4 ± 6.5</td>
</tr>
<tr>
<td>Wear rate [10$^5$ g/m]</td>
<td>108 ± 1.2</td>
<td><strong>81 ± 2.4</strong></td>
<td>88 ± 4.8</td>
<td>83 ± 5.8</td>
<td>91 ± 3.2</td>
</tr>
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4. CONCLUSION

The performed experiments showed that the ceramic materials can be successfully sprayed by the technology of flame spraying. In the process of parameters optimization, the parameter with the most significant effect showed to be the spraying distance. Mutual ratio between the amount of oxygen and fuel
has a negligible effect on the evaluated parameters. The sets of parameters, recommended for spraying of each material, were found and will be further use for commercial purposes.

ACKNOWLEDGEMENT

The paper was written thanks to the institutional support for a long-time development of a research institute.

REFERENCES


