Comparative Analysis of Mechanical Properties of WC-Based Cermet Coatings Sprayed by HVOF onto AZ31 Magnesium Alloy Substrates

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ABSTRACT
Magnesium alloys are very interesting engineering materials due to their very high strength to density ratio (the best among metallic alloys). However, because of low hardness as well as low resistance against erosion, abrasion and corrosion, their applications in the industry is very limited. In order to improve mechanical performances, deposition of hardening coating by thermal spraying was proposed. In this work, the WC-based coatings with different binder (Co or Ni) and co-hardening additives (Cr or Cr₃C₂) manufactured by high velocity oxy-fuel (HVOF) were studied. These coatings were deposited onto AZ31 magnesium alloy. The crucial problem is obtaining good-adhered coating without damage the substrate, because of relatively low temperature resistance of magnesium alloys (about 300 °C). To solve this problem, HVOF method, which is low temperature and high velocity, was proposed. Also an important role plays process parameters (e.g. spray distance, fuel medium, type of nozzle). The goal of the study was to compare three types of cermet coatings manufactured from commercially available powders (WC-Co, WC-Co-Cr and WC-Cr₃C₂-Ni) in terms of their microstructure features, microhardness, instrumented indentation and fracture toughness. Results revealed that selected process parameters made it possible to obtain well-adhered coating with good fulfillment of the surface unevenness of the AZ31 substrate. The most noticeable effect was influence of cobalt matrix on higher hardness (1.4 – 1.6 GPa) and Young modulus (330 – 340 GPa) of deposited coatings in compare to the nickel matrix ones (1.2 GPa and 305 GPa, respectively). The same trend was observed in case of fracture toughness, c.a. 6.5 MPa·m⁰.⁵ for Co-matrix and 4.9 MPa·m⁰.⁵² for Ni-matrix.

Keywords: cermet coating, HVOF spraying, magnesium alloy AZ31, microstructure, mechanical properties, indentation test, fracture toughness, microhardness, tungsten carbide
combustion chamber. At the same time feedstock material is supplied in the form of a powder into stream. This ensures that gas and material are quickly discharged under high pressure through the nozzle. Due to the working conditions and requirements for coatings, they can have various chemical compositions [14, 15]. Materials used to improve abrasive properties are most often composite powders that improve substrate wear resistance in many applications: regeneration of machine parts, such as WC-Co, WC-Co-Cr, NiCr-Cr,C$_2$, WC-CrC-Ni. In order to improve abrasive and corrosive properties at elevated temperatures powders NiCr-Cr$_3$C$_2$ or NiCr-Cr$_3$C$_2$ with additional modifications, e.g., Cr$_3$C$_2$-TiC-NiCr, WC-Cr$_3$C$_2$NiCr or Ni are used [16-19]. Especially WC-based powders are widely used as they are characterized by a very high hardness compared to most cerments, and addition of, for example, Cr and Co as binding ingredients improves their strength and provides better coatings adhesion. In the case of sprayed coatings from Cr$_3$C$_2$-NiCr powders, plastic NiCr phase is the matrix, and the reinforcement is hard Cr$_3$C$_2$ particles, which are resistant to abrasion [20-24].

The state of the art on the field of HVOF spraying includes deposition on the structural alloy steels, stainless steels, nickel alloys [25-27]. Relatively new and not deep investigated group of the substrate are light metal alloys. A proposed in this paper, AZ31 magnesium alloy with poor mechanical properties could be a good candidate for novel type of substrate for HVOF spraying [28-30].

In this paper, the mechanical properties of the tungsten carbide (WC) based coatings manufactured by HVOF on AZ31 magnesium alloy were examined in terms of their hardness, elastic modulus, fracture toughness, as well as microstructure and porosity level. The influence of the chemical composition on the above mentioned properties was detailed investigated.

**MATERIALS AND METHODS**

**Feedstock materials**

In this study as a coating material, three commercially available powders: (i) WC-Co-Cr (Höganas, Amperit 558.074); (ii) WC-Co (Höganas, Amperit 518.074) and (iii) WC-Cr$_3$C$_2$-Ni (Woka 3702-1) were used. The chemical composition of the feedstock powders is presented in the Table 1.

The particle size distribution was in the range 45–15 µm for each one. All powders were agglomerated and sintered. Figure 1 shows the typical scanning electron microscopy (SEM) image (Supra 35, Zeiss, Oberkochen, Germany) of the sprayed powders.

**Spraying process**

High Velocity Oxy Fuel (HVOF) method was used to deposit WC-based cermet coatings. The JP 5000 spray system Tafa (Indianapolis, USA) by RESURS (Warszawa, Poland) was used to manufacture coatings. The coatings were deposited on the magnesium alloy AZ31 with 5 mm in thickness. Before the spraying, the surfaces of the samples were sand blasted with corundum and ultrasonic cleaned in ethanol. The scheme of spraying and fundamental process parameters are presented in Figure 2.

**Microstructure and mechanical properties**

The deposited coatings were analysed using digital optical microscope Keyence VHX6000 (Keyence International). Observations were carried out of the coatings’ cross-sections. Samples in as-sprayed conditions have been examined in terms of surface roughness (Ra parameter). It was measured by stylus profilometer (Mahr Surf PS 10), according to the ISO 4288 standard. For each sample ten measurements were carried out. The porosity was assessed on the cross-sections, according to the ASTM E2109-01 standard. The micrographs taken at magnifications of 500x were used. To calculate porosity by image analysis method a software ImageJ was used. The microhardness of sprayed coatings was measured with Vickers indenter under the load of 2.94 N (HV0.3) using the HV-1000 hardness tester (Sinowon), according to the ISO 4516 standard. For each

<table>
<thead>
<tr>
<th>Table 1. Chemical composition of the HVOF feedstock powders</th>
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<tr>
<td><strong>Powder</strong></td>
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<tr>
<td>WC-Co-Cr</td>
</tr>
<tr>
<td>WC-Co</td>
</tr>
<tr>
<td>WC-Cr$_3$C$_2$-Ni</td>
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coating 10 indentations were made, then average values and standard deviations were calculated. Subsequently, the instrumental indentation tests were carried out using NHT nanoindentor (Anton Paar) with Berkovich indenter, according to the ISO 14577-4 standard. Instrumental hardness was determined with the value of maximum load equal to 500 mN, according to Oliver-Pharr methodology [31] (Fig. 3).

On the other hand, Young modulus values were calculated from slope of unloading curves for indents with different maximum loads (in present study from 50 up to 500 mN, with step equal to 50 mN). This methodology was originally proposed by Chicot. Fracture toughness was estimated in method based on measurements of cracks length, which occur in the coating material after Vickers indenter penetration. This methodology based on Palmqvist observation. The scheme of cracks and equations are presented in Figure 4. The value of maximum load was equal to 98.1 N (10kG). For each coating seven indents were made, then average values and standard deviations were calculated.
RESULTS AND DISCUSSION

Coatings microstructure

The microstructures of the sprayed coatings are presented in Figure 5. It could be seen that all coatings are dense, homogenous and well adhered to the substrate. The average thickness of all coatings varied from about 180 up to 250 µm. For all samples, at the coatings-substrate interface it could be seen well adhered coating material, which good filled substrate surface irregularities. On the cross-section views a good mechanical interlocking with the substrate [34, 35]. Such type of structure is a result of the HVOF spraying technology [36].

The surface of the coatings are relatively smooth. The results of the surface roughness as well as coatings porosity are collected in Table 2. The higher surface roughness (Rₐ) was found for WC-Cr₃C₂-Ni coating, which probably is related to the two types of hard particles and relatively soft and plastic nickel matrix. The porosity level is comparable with other types of such coatings in literature and it is typical around 1.5 up to 3.0 vol.% [37, 38]. Another factor is spraying set-up and HVOF gun. Slight differences in the gun construction could result in the minor discrepancy of coatings microstructure.
Mechanical properties

Figure 6 presented the comparison of conventional microhardness (Fig. 6a) and instrumental hardness (Fig. 6b) of deposited coatings. The highest values exhibit WC-Co (1296 HV0.3), whereas the lowest ones are for WC-Cr$_3$C$_2$-Ni (989 HV0.3) coatings. It may be due to the high content of WC in WC-Co coating and the most compact structure. On the other hand, WC-Cr$_3$C$_2$-Ni coating exhibit the lowest porosity and the nickel matrix has lower hardness than cobalt one [36, 39].

Results presented in Table 3 showed, that the Young modulus strongly influences on fracture toughness. In general, for all coatings the cracks length were almost the same dimension. However, the important factors for fracture toughness estimation were also hardness, as well as porosity. Results obtained in current studies are slightly different with some literature data [40-42]. It could be explained due to the fact, that these coatings were sprayed with different set-up and slightly differences in the parameters could

### Table 2. Comparison of the surface roughness and porosity of manufactured coatings

<table>
<thead>
<tr>
<th>Coating</th>
<th>Surface roughness $R_a$, µm</th>
<th>Porosity, vol.%</th>
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<tbody>
<tr>
<td>WC-Co-Cr</td>
<td>4.5±0.1</td>
<td>2.9±0.7</td>
</tr>
<tr>
<td>WC-Co</td>
<td>4.2±0.2</td>
<td>2.6±0.5</td>
</tr>
<tr>
<td>WC-Cr$_3$C$_2$-Ni</td>
<td>5.4±0.4</td>
<td>1.9±0.5</td>
</tr>
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### Table 3. Comparison of the fracture toughness and Young modulus of manufactured coatings

<table>
<thead>
<tr>
<th>Coating</th>
<th>Fracture toughness, MPa·m$^{1/2}$</th>
<th>Instrumental Young modulus, GPa</th>
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<tbody>
<tr>
<td>WC-Co-Cr</td>
<td>6.42±0.87</td>
<td>341</td>
</tr>
<tr>
<td>WC-Co</td>
<td>6.65±0.62</td>
<td>333</td>
</tr>
<tr>
<td>WC-Cr$_3$C$_2$-Ni</td>
<td>4.91±0.57</td>
<td>305</td>
</tr>
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influence on final properties. In case of fracture toughness, insignificantly higher values in present studies (see Table 3), than in literature (from 4.0 up to 5.0 MPa·m$^{1/2}$) [43,44]. These differences could be explained by higher porosity level (in range from 2.0 up to 3.0 vol.%) instead 1.5% or below, which could stopped cracks propagation.

CONCLUSIONS

Three WC-based coatings (WC-Co-Cr, WC-Co and WC-Cr$_3$C$_2$-Ni) were deposited by HVOF method on AZ31 magnesium alloy. The following findings can be summarized:
1. All coatings have been successfully deposited, the coating-substrate interface was clear, without discontinuities and with good mechanical interlocking between coating and substrate.
2. Microscopic observation revealed dense structure (porosity level below 3.0 vol.% and smooth surface ($R_a$ below 5.5 µm) of as-sprayed samples.
3. Microhardness and instrumental hardness measurements showed the same tendency (WC-Co > WC-Co-Cr > WC-Cr$_3$C$_2$-Ni). Moreover, they confirmed that coatings based on cobalt matrix exhibit higher microhardness (1198 HV0.3 for WC-Co-Cr and 1296 HV0.3 for WC-Co) than ones based on nickel matrix (989 HV0.3 for WC-Cr$_3$C$_2$-Ni).
4. Fracture toughness value was the highest for WC-Co coating (6.65 MPa·m$^{1/2}$), whereas the highest value of instrumental Young modulus was find for WC-Co-Cr coating (341 GPa).
5. Based on the above results, the most promising candidate for further dry sliding, erosion and cavitation resistance coating could be WC-Co-Cr one. It is characterized by considerable hardness, relatively good fracture toughness and high value of elastic modulus.

Acknowledgement

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