TRIBOLOGICAL PROPERTIES OF WC-Co/NiCrBSi AND Mo/NiCrBSi PLASMA SPRAY COATINGS UNDER BOUNDARY LUBRICATION CONDITIONS

Aleksandar VENCL¹*, Mihailo MRDAK², Pavol HVIZDOS³

¹University of Belgrade, Faculty of Mechanical Engineering, Belgrade, Serbia
²Research and Development Centre, IMTEL Communications a.d., Belgrade, Serbia
³Institute of Materials Research, Slovak Academy of Sciences, Košice, Slovakia

*Corresponding author: avencl@mas.bg.ac.rs

Abstract: The tungsten carbide based WC-Co/NiCrBSi (50/50) and molybdenum based Mo/NiCrBSi (75/25) coatings were investigated under boundary lubricated sliding conditions, and their tribological properties were analysed and compared. These two coatings are in service for a long time, but there are very few papers dealing with their tribological properties, especially in lubricated sliding conditions. The NiCrBSi self-fluxing alloy is one of the popularly used materials for thermal sprayed coating, with relatively high hardness, reasonable wear resistance and high temperature corrosion. Tungsten carbide (WC) is one of the most widely used commercial hard coating materials, and is added to the NiCrBSi coating to improve its hardness and wear resistance. Molybdenum (Mo) is added to the NiCrBSi coating to reduce its coefficient of friction, i.e. to improve its dry sliding wear resistance. The results showed that WC-Co/NiCrBSi coating was more wear resistant, but caused higher wear of the counter-body material. Coefficients of friction were similar for both coatings.

Keywords: coatings, tungsten carbide, molybdenum, atmospheric plasma spraying, boundary lubrication, friction, wear.

1. INTRODUCTION

Thermal spraying is widely used coating deposition method because it presents process flexibility and coating quality in combination. It represents a group of techniques for the coating deposition in which both, thermal and mechanical energy is applied for deposition of the material. There are several different processes for thermal spray coating deposition, and the main classification, into two categories, can be performed according to the thermal energy source used for melting of the feedstock material: flame (combustion) and electrical (electrical discharge) energy. The most widely used processes for thermal spray coating deposition are: flame spraying, electric arc wire spraying, atmospheric plasma spraying and high velocity oxygen fuel spraying [1].

One of the popularly used materials for hard thermal sprayed coating is a NiCrBSi self-fluxing alloy. This coating have several interesting properties, e.g. relatively high hardness, reasonable wear resistance and high temperature corrosion [2]. However, numerous
studies have been undertaken with the aim of improving the wear resistance of this coating, and these studies have pointed in the direction of adding “hard” particles like (WC, NbC, Cr$_3$C$_2$, TiC, SiC, VC, WC-Ni) to the base formed by the secondary material [3]. Among commercial hard coating materials, tungsten carbide (WC) is the most widely used for wear resistance coating for its high hardness. Cobalt (Co) binder prealloyed tungsten carbide powder was generally used to complementing its limited toughness [4], so the WC-Co powder particle consists of the hard tungsten carbide grain imbedded in tough cobalt matrix. The NiCrBSi self-fluxing coating performs well as a wear resistant coating under low stress. However, at higher stress in unlubricated sliding condition it begins to deform, which may cause seizure as the stress increases. Molybdenum (Mo) is added to the coating to reduce the coefficient of friction, thus, improving its dry sliding wear resistance [5]. In addition, Mo can form metallurgical bonding with many metals and decrease cracking sensitivity of coating in thermal spray processes [6].

The first powder used in this research (WC-Co/NiCrBSi) was a blend of powders composed of 50 wt. % hard phase constituent WC-Co and 50 wt. % self-fluxing alloy NiCrBSi. According to the powder manufacturer, deposited coating has high erosive and abrasive wear resistance. The WC-Co/NiCrBSi coatings are very dense, hard and smooth, with good adherence between coating and substrate. The second powder used in this research (Mo/NiCrBSi) was a blend of powders composed of 75 wt. % Mo and 25 wt. % self-fluxing alloy NiCrBSi. According to the powder manufacturer, deposited coating has high wear resistance, low coefficient of friction and good scuffing resistance. It is compatible with the most of the materials, especially with iron base alloys. The Mo/NiCrBSi coatings are homogenous with less than 3 % of porosity and with good adherence between coating and substrate. Both coating can be used unfused, resulting in no metallurgical bond to the substrate.

These two coatings are in service for a long time, but there are very few papers dealing with WC-Co/NiCrBSi [4,7-9] and Mo/NiCrBSi [5,6,10-13] tribological properties, especially in lubricated sliding conditions [14]. The aim of this paper is to investigate and compare the tribological properties of these two coatings under lubricated sliding conditions.

2. EXPERIMENTAL DETAILS

2.1 Materials

Two spray powders were used in the experiment, i.e. tungsten carbide based powder (Metco 34F) and molybdenum based powder (Metco 505). The chemical compositions of the powders are shown in Table 1.

The Metco 34F powder is composed of a fine tungsten carbide-cobalt powder blended with a fine nickel-chrome self-fluxing alloy powder. It contains 50 wt. % of tungsten carbide-cobalt and 50 wt. % of nickel-chrome self-fluxing alloy. Particle granulation of this spray powder blend was –53/+15 µm. The Metco 505 powder is a blend of molybdenum and nickel-chrome self-fluxing alloy. The share of the individual powder in the blend was 75 wt. % of molybdenum and 25 wt. % of nickel-chrome self-fluxing alloy. This spray powder blend shows spherical morphology with particle granulation –90/+15 µm. The substrate material was a stainless steel (EN X15Cr13). This substrate material was used without any heat treatment. For the convenience, coatings attained using Metco 34F and Metco 505 powders are hereafter referred to as 34F and 505, respectively.

<table>
<thead>
<tr>
<th>Table 1. Chemical composition (wt. %) of used powders</th>
</tr>
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<tbody>
<tr>
<td>Powder*</td>
</tr>
<tr>
<td>Metco 34F</td>
</tr>
<tr>
<td>Metco 505</td>
</tr>
</tbody>
</table>

*Commercial brand names of Metco Inc.
Atmospheric plasma spraying (APS), with Plasmadyne SG-100 plasma spray gun, was utilized in the experiment, for both coatings deposition. In both cases specimen holder was rotated at constant speed of 500 mm/s, while the traverse speed of a spraying gun was maintained constant at 4 mm/s. Fusing of both coatings after the deposition was not performed, i.e. coatings were tested in unfused conditions. Before the spraying process, the surface of the substrates was activated and preheated. Activation (roughening) was done with white fused alumina (Al$_2$O$_3$) using particle sizes of 700 – 1500 μm. Before the deposition, the substrates were preheated to 200 °C. The coating thickness for all specimens (after deposition and machining) was approximately 300 μm. The detailed spray parameters are summarised in Table 2 [15].

Table 2. APS spray parameters values used for coating deposition

<table>
<thead>
<tr>
<th>Spray parameter</th>
<th>Coating 34F</th>
<th>Coating 505</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary plasma gas (Ar), l/min</td>
<td>47</td>
<td>47</td>
</tr>
<tr>
<td>Secondary plasma gas (H$_2$), l/min</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>Electric current, A</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>Electric potential difference, V</td>
<td>64</td>
<td>64</td>
</tr>
<tr>
<td>Powder carrier gas (Ar), l/min</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Powder feed rate, kg/h</td>
<td>1.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Spray distance, mm</td>
<td>125</td>
<td>130</td>
</tr>
</tbody>
</table>

2.2 Microstructure analysis and hardness testing

The microstructure of the coatings was analyzed with scanning electron microscope (SEM), equipped with energy dispersive spectrometer (EDS), where the coatings were sectioned perpendicular to the coated surface. Metallographic samples were prepared in a standard way, applying grinding and polishing, with no etching.

Measurements of the surface microhardness (HV 0.3 and HV 1) were performed on surface of the samples (not on cross-section) using Vickers microhardness tester under the loads of 300 g and 1 kg, and dwell time of 5 s. Microhardness HV 0.3 is the standard parameter for thermal sprayed coatings, while the microhardness HV 1 is measured to diminish the influence of different hardness of coatings phases/layers (WC-Co and NiCrBSi, i.e. Mo and NiCrBSi). At least five measurements were made for each sample in order to eliminate possible segregation effects and to obtain a representative value of the coating microhardness.

2.3 Tribological testing

Tribological testing were carried out on block-on-disc tribometer, under lubricated sliding conditions, in ambient air, at room temperature (about 25 °C), in accordance with ASTM G 77 standard [16]. A schematic diagram of the tribometer is presented in Figure 1. Rectangular blocks (6 × 16 × 12 mm) of the tested coatings were used as wear test specimens. The disc of 45 mm diameter and 10 mm thickness was made of steel C60E (428.6 HV 1). The length of the line contact between the block and the disc was 6 mm. Lubrication was provided by the rotation of the disc which was sunk into the oil container (Fig. 1). The lubricant was mineral engine oil (SAE 15W-40, ACEA E3). Surface roughness of blocks and discs was approximately $Ra = 0.3$ and 0.5 μm, respectively.

Figure 1. Schematic diagram of block-on-disk testing

Before and after testing, blocks and discs were degreased and cleaned with benzene. Wear scars on blocks were measured according to [16] with accuracy of 0.05 mm, after each test, to calculate the volume loss. Discs were weighed with accuracy of 0.1 mg, before and after each test, to calculate the mass loss. Mass loss is then converted to volume loss using the known value of disc density (7.85 g/cm$^3$).
Values of the oil temperature, coefficient of friction, normal and friction force were continuously monitored during testing and through data acquisition system stored in the PC. After testing, worn surfaces of blocks were examined using the SEM/EDS analysis.

The tests were carried out under the following conditions: sliding speed of 0.5 m/s, sliding distance of 3000 m and normal load of 400 N. In order to achieve a higher confidence level in evaluating test results, at least three replicate tests were conducted for each coating.

3. RESULTS AND DISCUSSION

3.1 Microstructure and microhardness

The microstructures of the investigated coatings (Fig. 2) were typical for thermal spray coatings and consist of elongated splats of molten powder, which form a curved lamellar structure, and oxide layers and inclusions in between [1]. Microstructure of the coating 34F (Fig. 2a) consists of WC-Co and NiCrBSi layers, which is confirmed with the EDS analysis (Figs. 3a and 3b). Presence of micropores was also noticed (denoted with arrows in Fig. 2a). In the microstructure of coating 505 (Fig. 2b), two distinct layers could be also clearly noticed. There are the Mo layers which form a base of the coating, and the NiCrBSi layers which are evenly distributed between the Mo layers. This is also confirmed with the EDS analysis (Fig. 3c and 3d). Micropores, as well as, interlamellar pores were noticed in coating 505 (denoted with arrows in Fig. 2b). Detail microstructural analysis of the obtained coatings is presented elsewhere [15,17,18].
The results of hardness measurements are shown in Figure 4. As expected, hardness values measured with higher load (HV 1) were slightly lower. The variation in hardness for both coatings was satisfactory (about 5%). Microhardness values of coating 34F (WC-Co/NiCrBSi) was higher than values of coating 505 (Mo/NiCrBSi) due to the presence of hard WC phase. Obtained values are in correlation with cross-section values of the microhardness, taking into account that the hardness of NiCrBSi layers is significantly lower than the hardness of WC-Co layers [17], i.e. significantly higher than the hardness of Mo layers [18]. No matter what, hardness of discs (428.6 HV 1) was lower than both coatings and than all coatings layers.

![Figure 4. Microhardness of tested coatings](image)

3.2 Tribological properties

Obtained average steady-state values of the coefficient of friction are presented in Figure 5. The results indicate good repeatability of the test, i.e. standard deviations were less than 8 %. The lubricant temperature was also continuously monitored during the tests. Since it was not controlled, it was rising during the tests and reaches the near steady-state values at the end of the tests. These near steady-state values are used to calculate the temperature rise during each test, having in mind that the lubricant temperature at the beginning of the tests was close to room temperature (about 25 °C). The average values of these temperature rises are also presented in Figure 5.

![Figure 5. Steady-state values of the coefficient of friction and lubricant temperature rise during testing](image)

Values of both coefficients of friction correspond to the approximate experimental values for contact pairs under boundary lubrication conditions, which are from 0.05 to 0.15 [19,20]. According to the elastohydrodinamic theory for line contact, calculated lubricant minimal film thickness were very low (approximately 0.3 μm) for both contact pairs. This also suggest that the sliding was performed in the boundary lubrication regime, since the approximate values of the surface roughness of blocks and discs was approximately $Ra = 0.3$ and 0.5 μm, respectively. Since most of the energy lost due to the friction is released as heat, higher coefficient of friction will induce higher temperature. This explains the correlation between these two values obtained in this study for different contact pairs (Fig. 5).

Coefficient of friction and oil temperature change during the test were similar in all tests and for both contact pairs. Between two contact pairs, coating 505 (Mo/NiCrBSi) gives slightly lower coefficient of friction. It is, most probably, due to the presence of Mo in this coating, which should decrease the dry sliding friction [5]. Relatively high value of the coefficient of friction that gives coating 34F (WC-Co/NiCrBSi) could be due to the presence of protruded hard WC phase and unfavourable proportion of the components in powder blend. Kekes et al. [9] investigated, under dry sliding conditions, WC-Co-Cr/NiCrBSi coatings with different fractions (from 0 to 100 wt. %) of WC-
Co component, and showed that 50 wt. % of WC-Co-Cr give the highest coefficient of friction. Values of the wear rate of both of contact pair elements (block and disc) are presented in Figure 6. The wear rate of counter-body (disc) is very meaningful when the total clearance between tribological elements is of importance, and that is why it was also calculated. Taking into account significant differences in structure homogeneity of the coatings (Fig. 2), the repeatability of the wear rates of blocks, in terms of standard deviations, is satisfactory (within 10 %). Since the wear values were not measured continuously, i.e. during the test, the results in Figure 6 show total wear rates, which are usually higher than steady-state values.

Taking into account normal load of 400 N, wear factor values could be calculated [21] as: $7.6 \times 10^{-9}$ mm$^3$/Nm (coating 34F), $9.7 \times 10^{-9}$ mm$^3$/Nm (coating 505), $2.9 \times 10^{-7}$ mm$^3$/Nm (disc in contact with coating 34F) and $1.5 \times 10^{-7}$ mm$^3$/Nm (disc in contact with coating 505). These wear factor values (both for coatings, as well as, for steel discs) correspond to the literature data for metallic materials in sliding contact, under boundary lubricated condition, which are from $10^{-9}$ to $10^{-6}$ mm$^3$/Nm) [22]. It is interesting to notice that coating 34F wear less, but caused higher wear of the counter-body (disc) material.

Obtained wear values of investigated coatings (Fig. 6) are in correlation with their hardness values (Fig. 4), i.e. coating 34F (WC-Co/NiCrBSi) was harder and showed higher wear resistance, and vice versa. In the case of coating 34F, hard WC particles protruded from the matrix protected the matrix from wear. Something similar was observed, although in slurry erosive wear testing, by Lu et al. [8]. The protruded WC particles also caused higher wear of steel disc when it was in contact with coating 34F (Fig. 6). On the other hand, coating 505 (Mo/NiCrBSi) showed higher wear value due to the fact that this blend mixture of Mo and NiCrBSi powders do not show the best wear resistance under dry sliding conditions. Niranatlumpong and Koiprasert [5] investigated, under dry sliding conditions, Mo/NiCrBSi coatings with different fractions (from 0 to 100 wt. %) of Mo powder in the blend, and showed that 75 wt. % of Mo had the highest wear.

Disc wear rates were much higher than blocks wear rates in both cases (more than 37 and more than 15 times, for contact with coating 34F and with coating 505, respectively). This is partially due to the lower hardness of the discs and partially due to the high initial roughness of the discs. Taking into account the diameter of the discs (45 mm) and length of the line contact between the block and the disc (6 mm), wear rate of $1 \times 10^{-4}$ mm$^3$/m corresponds to the volume of the hollow cylinder of approximate thickness of 0.4 μm. This thickness corresponds very well to the initial roughness of the discs ($Ra = 0.5 \mu m$).

Wear mechanism analysis showed that the dominant wear mechanism was light two-body abrasion (Fig. 7). There is no evidence of the adhesive wear or plastic flow of the coatings material on the surface. Only shallow abrasive scratches can be noted in the sliding directions (denoted with black arrows in Fig. 7). Discs roughness was relatively high, but the hardness was much lower, so the main wear of the coatings was in the running-in period. Diagonal abrasive traces are consequences of machining (initial coating roughness). These machining traces are still visible on both coatings worn surfaces, suggesting low intensity of wear. Nevertheless, machining traces on coating 34F worn surfaces are more visible, confirming the lower wear of this coating.
Figure 7. Worn surfaces (SEM): (a) coating 34F and (b) coating 505; counter-body sliding directions are denoted with black arrows.
Worn surface of coating 34F was covered with small white particles (Figs. 7a and 8a). These particles are the result of larger WC particles fragmentation, which is confirmed with the EDS analysis (Spectrum 1 on Fig. 8a). The results of EDS analysis are shown in Table 3. These small and hard WC particles probably contributed, through the tree-body abrasion, to the higher wear of steel disc, when it was in contact with coating 34F (Fig. 6). Direction of WC fragmentation is the same as the direction of machining, so it is reasonable to conclude that the fragmentation mainly occurred before wear testing, i.e. during machining. These small WC particles were impressed into the softer NiCrBSi layers, which can be seen on SEM surface topography image (Fig. 8b). Presence of protruded larger WC particles, which protected the matrix, could be noticed on the same image.

Figure 8. Worn surface (SEM) of coating 34F: (a) backscatter electron detector image and (b) surface topography image

Figure 9. Worn surface (SEM) of coating 505: (a) backscatter electron detector image and (b) surface topography image
Table 3. Results of EDS analysis on the worn surfaces of coatings (chemical composition are in wt. %)

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>W</th>
<th>Co</th>
<th>Mo</th>
<th>Ni</th>
<th>Cr</th>
<th>B</th>
<th>Si</th>
<th>Fe</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>78.8</td>
<td>1.7</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>19.5</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>–</td>
<td>–</td>
<td>68.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>31.2</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>–</td>
<td>–</td>
<td>5.2</td>
<td>53.8</td>
<td>12.3</td>
<td>–</td>
<td>3.4</td>
<td>2.3</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Analysis of the coating 505 worn surface showed presence of interlamellar pores and cracks (Fig. 7b). The cracks occurred mainly in the Mo-rich areas (Spectrum 2 on Fig. 7b), but also in harder Ni-rich areas (Spectrum 3 on Fig. 9a). In the case of coating 505, worn surface topography did not show any protruded particles (Fig. 9b). This means that the whole surface was in contact, having as a consequence higher wear of this coating.

4. CONCLUSIONS

In this study, the tribological properties of WC-Co/NiCrBSi and Mo/NiCrBSi plasma spray coatings under sliding lubrication conditions were investigated and compared. Both coatings showed microstructures typical for thermal spray coatings, which consist of elongated splats of molten powder, which form a curved lamellar structure, and oxide layers and inclusions in between.

Coefficient of friction values suggest that the sliding was performed in the boundary lubrication regime. Between two contact pairs, Mo/NiCrBSi coating gives slightly lower coefficient of friction, most probably due to the presence of Mo in this coating, and consequently slightly lower rise of lubricant temperature during testing.

The wear values showed that WC-Co/NiCrBSi coating was more wear resistant than Mo/NiCrBSi coating, but caused higher wear of the counter-body material. Higher wear resistance of WC-Co/NiCrBSi is due to the higher hardness of this coating, as well as due to the presence of protruded hard WC particles, which protected the softer matrix. The dominant wear mechanism for both coatings was light two-body abrasion.

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