ANALYSIS OF CrAgN COATING ON VANADIS 6 STEEL AFTER PIN-ON-DISC TESTING

Jana BOHOVIČOVÁ, Peter JURČI, Mária HUDÁKOVÁ, Ľubomír ČAPLOVIČ, Martin SAHUL, Pavel BÍLEK

Faculty of Materials Science and Technology of the STU, Department of Materials, Trnava, Paulínská 16, 91724 Trnava, Slovak Republic, jana.bohovicova@stuba.sk

Abstract
Samples made from Vanadis 6 PM ledeburitic tool steel were surface machined, ground, and mirror polished. They were heat treated and coated with CrAgN by magnetron sputter deposition at the Hauser Flexicoat 850 device. PVD coatings contained 3% of Ag. Tribological testing using a pin-on-disc apparatus has been realized at elevated temperatures: 300, 400 and 500 °C, respectively. Al₂O₃ and bronze balls were used as counterparts. Wear tracks after pin-on-disc testing were analyzed by scanning electron microscope and microanalysis. The experiments have shown strong dependency of tribological parameters on temperature. In the case of Al₂O₃ counterpart, the friction coefficient of CrAg3N was 0.238–0.168 from 300 °C to 500 °C. Testing against CuSn6 bronze ball gave generally lower friction coefficient. A decrease of wear ratios was recorded at elevated temperatures. EDS analysis detected partial removal of the coating in case of 300 °C and 400 °C while the coating was completely from the substrate during the testing at 500 °C.

Keywords:
Vanadis 6 cold work steel, PVD, chromium nitride, silver addition, pin-on-disc testing

1. INTRODUCTION
Multi-functional composite coatings containing soft lubricious phases within hard wear-resistant matrix have been studied extensively in recent years due to their promise for tribological performance in aggressive environments and/or at elevated temperatures. In particular, inclusions of noble metals such as Ag and Au show promise as solid lubricating phases in carbide, oxide, and nitride matrices, as they possess sufficiently low shear strength over a suitably wide temperature range as well as stable thermochemistry allowing them to be used in both the ambient air and the vacuum [1]. For example, Mulligan et al. [4] and Kutschej et al. [5] recently combined CrN with silver, to produce CrN–Ag self-lubricating films. Silver being extremely mobile diffuses out of the matrix to be transferred to the surface in order to maintain a low friction coefficient at high operating temperatures (≈600 °C). The self-lubricating nature of such adaptive coatings has the potential to extend the service lifetime in numerous moving mechanical assemblies that exist in many applications, including air and space industries as well as the manufacturing and tooling sectors [4-9]. The advantage of a wear test, when compared to indentation or scratch testing, is that it can give a measure of the lifetime of a particular coating-substrate system. In many applications of coatings, the resistance to wear can be more important than the load required to permanently damage the material. The properties of the coating being tested and the substrate on which it has been deposited will influence the friction signal when the coating is worn through: in some cases this signal will rise dramatically, in others it may drop. Whichever the change, the breakdown of the coating will nearly always manifest itself as a sharp change from the steady sliding state [10].
2. EXPERIMENTAL PROCEDURE
The experimental substrate samples were made from the ledeburitic steel Vanadis 6 with nominally 2.1 %C, 1.0 %Si, 0.4 %Mn, 6.8 %Cr, 1.5%Mo, 5.4 %V and Fe as balance. After rough machining to the semi-final dimensions, the samples were subjected to standard heat treatment procedure giving a final hardness of 724 HV 10. After the heat treatment, the samples were fine ground and polished up to the mirror finish. The CrAgN - coatings were deposited in a magnetron sputter deposition system, in a pulse regime with a frequency of 40 kHz. Two targets, opposite positioned, were used. For the deposition of silver containing films, one silver cathode (99.98% of purity) was inserted into the processing chamber instead of one chromium target. In these trials, the cathode output power was 5.8 kW on the chromium cathode. On the silver cathode, the output power was 0.1 kW in order to produce the silver content of 3 wt%. The deposition temperature was 500 °C. It was achieved by resistive heaters placed on internal walls of the processing chamber. The process was carried out in a low pressure atmosphere (0.15 mbar), containing pure nitrogen and argon (99.999 % of purity), in a ratio of 1:4.5.

Tribological properties of the coatings were measured using the CSM Pin-on-disc tribometer at a normal load of 1N, at elevated temperatures, up to 500 °C. Balls 6 mm in diameter, made from sintered alumina and CuSn6 bronze (as-cast structure, hardness of 149 HV 10) were used for testing. After the testing, the wear tracks were examined by scanning electron microscope (SEM) JEOL JSM-7600F and energy dispersive X-ray analysis (EDX). EDS linescans across the wear tracks were performed to evaluate microcompositional changes associated with tribological testing.

3. RESULTS AND DISCUSSION
Table 1 shows an overview of the friction coefficients $\mu$ resulted from testing at a room temperature and elevated temperatures. CrAg3N films formed at 500 °C had average friction coefficient of 0.373 when the $\text{Al}_2\text{O}_3$ ball was used for the testing at a room temperature. Testing against CuSn6-bronze at a room temperature gave lower friction coefficient. At elevated temperatures, the difference in $\mu$ became less significant but, excepting the testing temperature of 400 °C it is valid that a silver addition of 3 wt % tended towards lowering of the friction coefficient. Mulligan et al. [1] reported a slightly positive effect of the addition of Ag into the CrN. However, they added 22 at.% Ag, which is approximately 10 times higher concentration than that used in our experiments. Additions of various Ag contents into CrAlN films were studied by Basnyat et al. [2]. They established a beneficial effect of Ag on the friction coefficient against alumina at room temperature, but only up to the Ag-content of 9 at.%. Finally, Yao et al. [3] also determined a beneficial effect of a small Ag content in the CrN on the lowering of the friction coefficient against a low carbon steel sphere. However, the loading applied in their investigations was also much higher, which makes the results incomparable with our measured data.

<table>
<thead>
<tr>
<th>Coating / Testing temperature [°C]</th>
<th>CrAg3N/500 °C</th>
<th>Al$_2$O$_3$</th>
<th>CuSn6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature</td>
<td></td>
<td>0.373</td>
<td>0.261</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>0.238</td>
<td>0.222</td>
</tr>
<tr>
<td>400</td>
<td></td>
<td>0.160</td>
<td>0.246</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td>0.168</td>
<td>0.165</td>
</tr>
</tbody>
</table>
Lowered friction coefficient $\mu$ of silver containing films is reflected in wear ratios measured by the pin-on-disc testing, Table 2. This statement is valid for 3 wt% Ag containing films, in particular, where substantial decrease of wear ratios was recorded at elevated temperatures.

Table 2 Wear ratio at ambient and elevated temperatures, alumina used as a counterpart [11]

<table>
<thead>
<tr>
<th>Coating / Testing temperature [°C]</th>
<th>CrAg3N/500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature</td>
<td>3.65x10^{-13}</td>
</tr>
<tr>
<td>300</td>
<td>8.405x10^{-12}</td>
</tr>
<tr>
<td>400</td>
<td>9.927x10^{-12}</td>
</tr>
<tr>
<td>500</td>
<td>1.522x10^{-11}</td>
</tr>
</tbody>
</table>

3.1 Wear at 300 °C

Fig. 1 shows the wear scar after testing at 300 °C against a counterpart made from $\text{Al}_2\text{O}_3$. There are many parallel lines oriented along the sliding direction on the coated material. EDS analysis shown the presence of iron and vanadium (base elements of steel) on the surface in some sites while both the high chromium content and the silver content have been established in other sites. These results confirm that partial removal of the coating from the substrate has commenced, whereas the area portion, where the removal took place, makes of about 25%.

3.2 Wear at 400 °C

Examination of the worn surface after testing at 400 °C (Fig. 2) against a counterpart from $\text{Al}_2\text{O}_3$ revealed relatively smooth wear track. We did not observe any transfer from the ball material onto the coating. EDS analysis indicated the presence of iron and vanadium on the surface inside the wear scar. It indicates that a partial coating removal commenced in a way similar to the testing at a temperature of 300 °C.
Fig. 2 SEM micrograph of the wear scare produced by the testing against Al₂O₃ at 400 °C and corresponding EDS maps of chromium, iron, silver and vanadium.

3.3 Wear at 500 °C

Figure 3 shows the SEM micrograph of wear scare produced by sliding of CrAg₃N-film grown at 500°C against a counterpart from Al₂O₃, at a temperature of 500 °C. The scare appears to be very smooth and is covered by some oxides. The EDS analysis of the material inside the scare indicates the main presence of vanadium and iron inside the wear track. On the other hand, the presence of silver has not been detected and, the chromium content is very low compared to that in the CrAg₃N-film. Based on these findings it is obvious that the coating material was removed almost completely from the substrate during the testing.

Fig. 3 SEM micrograph of the wear scare produced by the testing against Al₂O₃ at 500 °C and corresponding EDS maps of chromium, vanadium, silver and iron.
3.4 Wear against CuSn6

Investigation of the wear scare after testing at a temperature of 400 °C against CuSn6, Fig. 4, fixed relatively smooth surface inside the scare. However, there was a considerable material transfer from the counterface to the specimen’s surface detected. It should be noticed that such a material transfer has been detected for the samples tested at 300 and 500 °C, respectively, also. The transferred particles were analyzed by EDS analysis and it has been confirmed that it is the bronze which is presented on the surface inside the wear scare, Fig. 4. No other type of the coating damage has been observed.

Fig. 4 SEM micrograph of the wear scare produced by the testing against CuSn6 at 400 °C and corresponding EDS maps of chromium, vanadium, silver, iron and copper.

CONCLUSIONS

The friction and wear characteristics of the CrAg3N coatings prepared by magnetron sputter deposition method have been examined at different temperatures and with different counter-part materials. The results can be summarized as follows:

The friction coefficient decreased with increasing testing temperature rapidly when alumina ball has been used as a counterface while the decrease of the μ was moderate for the counterpart made from the CuSn6-ball used as a counterface.

The coating was partly removed from the substrate when tested at temperatures 300 °C and 400 °C, respectively, while the coating disappeared from the substrate almost completely at 500 °C, when alumina has been used as a counterface.

One can suggest that it is the softening of the CrAg3N plays a dominant role in the temperature behavior of the coating against alumina.

No removal or other coating damage has been established after sliding against the CuSn6-ball, but considerable material transfer from the ball to the sample has been detected. This is due to very low shear strength of the CuSn6, especially at higher temperatures.
ACKNOWLEDGEMENTS

This publication is the result of the project implementation: CE for development and application of advanced diagnostic methods in processing of metallic and non-metallic materials, ITMS:26220120048, supported by the Research & Development Operational Programme funded by the ERDF. This research was supported by the grant project VEGA 1/1035/12.

REFERENCES