CrAg7N NANOCOMPOSITE COATINGS DEPOSITED OF Cr-V LEDEBURITIC STEEL

Pavel BíLEK, Peter JURČI, Mária HUDÁKOVÁ, Jana BOHOVIČOVÁ, Jana SOBOTOVÁ

Abstract

Samples made from Vanadis 6 PM ledeburitic tool steel were surface machined, ground and mirror polished. Prior the deposition, they were heat treated to a hardness of 60 HRC. CrAg7N-coatings were deposited by magnetron sputtering technique, using pure Cr and Ag targets, in a composite low pressure nitrogen/argon atmosphere and at a temperature of 500 °C. The coatings have an average thickness of 4.3 μm. They grew in a very well visible columnar manner, but, individual silver agglomerates were visible along the columnar crystals, also. The average size of silver agglomerates lies well below 50 nm, e.g. one can suggest that they are capable to be solved and release the Ag atoms to be migrated to the free surface during thermal exposition. The coatings had a good adhesion on the surface – the first critical loads, established by scratch-testing method, ranged between 30 and 39 N.

Keywords: Nanocomposite coatings, Solid lubricant, CrN-Ag coatings, Surface morphology, Nanohardness.

1. INTRODUCTION

Chromium nitrides (CrN) have been extensively investigated in the applications of protective coatings due to their high hardness, good wear resistance as well as excellent corrosion and high temperature oxidation resistance [1-5]. They gained great scientific interest and industrial popularity due to those properties in copper machining, aluminium die casting and forming, and wood processing [6]. However, in many applications, the requirements on coated material surface cannot be met by such a single coating. A further development to adapt some of their properties to a desired value for specific applications is to produce composite coatings, where different material properties are combined and some new desired properties could be created [7-9].

Many research efforts have been dedicated to Cr-based ternary nitrides recently. The reported Cr-Ti-N, Cr-Al-N, Cr-W-N and Cr-Zr-N coatings actually present high hardness, high thermal stability or better corrosion resistance in comparison with CrN [10]. However, some of tribological properties of these films cannot be changed in a sufficiently wide range since they are given by the nature of the film compound itself. This is why the effect of self-lubrication has gained a great scientific importance in last few years. The main idea to develop self-lubricating and multi-purpose coatings is based upon the fact that commercially available lubricants (sulphides, oxides, graphite) exhibit considerable shortcomings and cannot be used effectively in tooling applications over sufficiently wide temperature range [11-13]. Soft noble metals on the other hand, posses stable chemical behaviour and can exhibit self-lubricating properties due to their low shear strength. Noble metal particle bring several benefits to the layer properties compared to metal oxides or graphite. They are stable up to relatively high temperatures, have low hardness and do not behave as abrasive particles. A common disadvantage of noble metals is their high cost, but this can be optimized to an acceptable level. Self-lubricating effect is based on incorporation of small amount of noble metals, mostly silver, into the basic CrN-film. Silver is completely insoluble in CrN and forms nano-particles in basic CrN-compound. Silver containing transition metal nitrides films have been extensively studied in recent years [14].
Chromium and chromium-vanadium ledeburitic steels are among the most typical substrates for the PVD coating. Due to their high wear resistance, good compressive strength, and hardness, these materials are applied in many industrial operations like metal cutting, wood working, fine blanking, drawing, etc. In these operations, material must meet various requirements. It has to withstand the compressive stresses, abrasive and/or adhesive wear, and also chipping and total tool collapse. To meet these demands, the steels must have an optional chemistry as well as phase constitution. In addition, proper heat treatment must be done before using tools made from Cr-V ledeburitic steels [15-17].

The current paper deals with the development of adaptive nanocomposite CrAgN coatings on the Vanadis 6 Cr-V ledeburitic tool steel. It describes and discusses the microstructure and the basic coating characteristics like hardness, Young’s modulus and adhesion for coating with 7 % content of silver.

2. EXPERIMENTAL

2.1 Materials and processing

The substrate material was the PM ledeburitic steel Vanadis 6 with nominally 2.1 % C, 1.0 % Si, 0.4 % Mn, 6.8 % Cr, 1.5 % Mo and 5.4 % V and Fe as a balance and soft annealed to a hardness of 21 HRC.

The samples used for the investigation were plates with dimensions of 50 mm x 10 mm x 10 mm, heat treated (austenitized at a temperature of 1050 °C, quenched in flow of nitrogen gas and double tempered for 2 hours at temperature 530 °C) to final hardness of 60 HRC and then finely ground and polished with diamond suspension up to a mirror finish.

The CrN/Ag-coatings were deposited by a Hauzer-Flexicoat 850 magnetron sputter deposition system in a pulse regime with a frequency of 40 kHz. Two targets, an Ag target (99.98 % purity) was used and pure chromium target (99.9 % Cr), positioned opposite one to another, were used. The output power on the Cr cathode was 5.8 kW and that on the Ag cathode was 0.21 kW. The processes were carried out in a low pressure atmosphere (0.15 mbar) containing nitrogen and argon in a ratio of 1:4.5.

The substrates were placed between the targets on rotating holders with a rotation speed of 3 rpm. Just prior to the deposition, the substrates were sputter cleaned in an argon low-pressure atmosphere for 15 min. The substrate temperature was 250 °C for the cleaning and 500 °C for the deposition. A negative substrate bias of 200 V was used for the sputter cleaning and that of 100 V for the deposition. The total deposition time was 6 h.

2.2 Investigation methods

The measurement of roughness was carried out on mirror finish samples and on samples with coatings by laser scanning confocal microscope Zeiss LSN 700. The analyses of the substrate microstructure, PVD-coatings investigation and the fractography were carried out using a JEOL JSM-7600F field emission scanning electron microscope (SEM) in BE-detection regime. Energy dispersive spectroscopy (EDS) was done on the same device at an accelerating voltage of 20 kV and standard working distance of 15 mm. For the examinations of the substrate, standard metallographic specimens were prepared and etched with Villela-Bain reagent. PVD layers were prepared for observation via a special method based on deep cooling of the samples in liquid nitrogen and subsequent breaking.

The nanohardness and the Young’s modulus (E) values of the coatings were determined using the instrumented nanoindentation test under a normal load of 60 mN using a Nanohardness tester TTX 2 CSM Instruments equipped with a Berkovich indenter. The indentation depth was kept to 10 % of the coating thickness to minimize the substrate effect. Fifteen measurements were made and the mean value and the standard deviation were then calculated.
The adhesion of the coating was examined using a CSM Revetest scratch-tester. The scratches were made under a progressively increasing load from 1 N to 100 N, with a loading rate of 50 N/min. A standard Rockwell diamond indenter with a tip radius of 200 μm was used. Five measurements were made on each specimen and the mean value and standard deviation of adhesion represented by the $L_{c1}$, $L_{c2}$, $L_{c3}$ and $L_{c4}$ critical loads, respectively, was calculated. The critical loads were determined by recording the signal of acoustic emission as well as by viewing the scratches on the SEM micrograph. The $L_{c1}$ critical load corresponds to the occurrence of the first inhomogeneities in the coating. The $L_{c2}$ and $L_{c3}$ correspond to another damages on the edge of the track. And finally the $L_{c4}$ critical load was determined as a load when all of the coating was removed from the substrate.

The hardness of the substrate was measured using the Rockwell C method (HRC). Five measurements were made on specimen and the mean value was calculated.

3. RESULTS AND DISCUSSION

The microstructure of the substrate material after applied heat treatment is shown in Fig. 1. The material consists of a matrix with fine carbides uniformly distributed throughout the matrix. SEM micrograph (Fig. 1a) shows that the matrix is formed with fine tempered martensite. The EDS-maps of chromium and vanadium (Fig. 1b and 1c) show that the carbides are of two basic types. Large particles, having a size up to 2 μm, are the $M_7C_3$ carbides, and the finer formations are the MC carbides. It was recently established [15,18] that $M_7C_3$ phase is chromium based that underwent dissolution in the austenite during heat processing, being responsible for the saturation of the austenite with carbon and alloying elements, which leads to high hardness of as-heat-treated material. Almost whole amount of MC phase remained undisolved. After the heat treatment, the average hardness of the material was 60 ± 0.3 HRC and the roughness of the surface before and after deposition was $Ra < 0.01 \mu m$.

![Microstructure of PM ledeburitic steel Vanadis 6 substrate after heat treatment: a-overview (SEM-BSE), b-EDS map of chromium from Fig. 1a, c-EDS map of vanadium from Fig. 1a.](image)

The thickness of CrAg7N coating was 4.3 μm (Fig. 2a). The film grew in a well visible columnar manner. This type of layer growth is typical for magnetron-sputtered CrN films at a wide range of processing parameters, as reported previously [19]. This result is in a good agreement with other reported results, also [20]. The addition of 7 % Ag into the CrN does not change the commonly known columnar morphology of such types of films and, in addition, the thickness of the film was practically the same as that of the pure CrN and that of coatings with 3 % of Ag [20]. SEM micrograph, Fig. 3a, made from the surface in the BE-detection regime, and corresponding EDS mapping of Cr, respectively Ag, Fig. 3b, respectively Fig. 3c show that silver forms individual grains along columnar grains as well as on the surface (Fig. 2b) at higher concentration. The average size of silver agglomerates lies well below 50 nm. Various authors have reported [21, 22] that individual silver agglomerates along the columnar crystals are capable to be solved and release the Ag atoms to be migrated to the free surface during thermal exposition and it could be responsible for self-lubrication effect (Fig. 3b and 3c).
The nanohardness of CrAg7N coating was 16.17 ± 1.93 GPa. This value is comparable to early reported results [20] for pure CrN and coating with 3 % of Ag, as seen in Table 1. Silver is very soft and could cause softening of the coating. However, no substantial effect of Ag addition on hardness was observed. Similar behavior can be found for measurement of Young’s modulus \( E \), Table 1. The Young’s modulus rather increases with an addition 7 % of Ag into the CrN coating, but the increase is only marginal when compared with the data published previously [20]. However, this slight increase in \( E \) is rather surprising because normally, a decrease of \( E \) is expected with an Ag – addition. Further examinations are required to better clarify this phenomenon.

**Tab. 1** Mechanical properties determined from nanoindentation measurements, values for CrN and CrAg3N are from previous work. * - data published previously [20].

<table>
<thead>
<tr>
<th>Coating</th>
<th>Hardness [GPa]</th>
<th>Young’s Modulus [GPa]</th>
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<tbody>
<tr>
<td>CrN*</td>
<td>16.79 ± 1.49</td>
<td>244 ± 15</td>
</tr>
<tr>
<td>CrAg3N*</td>
<td>15.97 ± 1.44</td>
<td>241 ± 9</td>
</tr>
<tr>
<td>CrAg7N</td>
<td>16.17 ± 1.93</td>
<td>263 ± 17</td>
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After the scratch test, the failure of CrAg7N coating proceeded with semi-circular tensile cracking (Fig. 4a). The coatings show a very brittle behavior. Even at the beginning of the scratches, there are many cracks visible, but the coating did not exhibit a tendency to be removed from the substrate, e.g. it has a good adhesion. The first inhomogeneities accompanied with the signal of acoustic emission occurred at a load 34.5 N \( (L_{c1}) \), (Fig. 4b). With increasing load more damages on the edge of track are visible, \( L_{c2} \) (Fig. 4c) and at load 52.9 N \( (L_{c3}) \) (Fig. 4c) occurred break substrate through the coating on the edge of the track. At a load of 79 N, the coating was removed from the substrate as documented the SEM micrograph in BE-detection.
regime (Fig. 5a). Corresponding EDS maps of chromium (Fig. 5b), silver (Fig. 5c), iron (Fig. 5d) and vanadium (Fig. 5e) show an interface where CrAg7N coatings crossing to substrate, steel Vanadis 6. On the surface of coating after exposure, smeared Ag particles are visible (Fig. 5f), which are probably responsible for better friction properties.

Fig. 4 Electron microscopy showing the failures after scratch testing: a-overview, b-L_{c1}, c-L_{c2}, d-L_{c3}.

Tab. 2 Adhesion properties determined from scratch test.

<table>
<thead>
<tr>
<th>Coating</th>
<th>L_{c1} [N]</th>
<th>L_{c2} [N]</th>
<th>L_{c3} [N]</th>
<th>L_{c4} [N]</th>
</tr>
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<tr>
<td>CrAg7N</td>
<td>34.52±3.31</td>
<td>44.36±1.58</td>
<td>52.85±1.62</td>
<td>79.04±2.19</td>
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Fig. 5 SEM micrograph showing the failures after scratch testing: a-L_{c4}, b-EDS map of chromium from Fig. 5a, c-EDS map of silver from Fig. 5a, d-EDS map of iron from Fig. 5a, e-EDS map of vanadium from Fig. 5a, f-surface after test.
CONCLUSIONS

The investigation of magnetron-sputtered CrAg7N-coatings deposited on Vanadis 6 ledeburitic steel has brought the following findings:

The coating grew in a typical columnar manner and had a thickness 4.3 μm. Columnar crystals are well visible on the cross-sectional micrographs. Individual silver agglomerates are located mostly on the crystal boundaries and their size was less than 50 nm.

The addition of 7% of Ag into the CrN film does not influence the hardness of the CrN negatively. On the other hand, the Young’s modulus has been established to be slightly higher than that of CrN or CrAg3N, which can be considered as rather surprising, because an opposite effect could be expected.

The adhesion of CrAg7N film can be considered as very good. This can be attributed to a good capability of the soft Ag particles to absorb the plastic energy, which makes the coating more resistant against delamination.

CrAgN coating of PM Cr-V ledeburitic steel Vanadis 6 is very promising way to increase its tribological properties at intermediate temperature. The addition of 7% of silver brings good adhesion properties without effect on hardness of coatings.

ACKNOWLEDGEMENTS

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