SELF-LUBRICATING THIN FILMS FOR TOOL STEELS

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Resume

Specimens made from Vanadis 6 cold work tool steel were machined, ground, heat processed by standard regime and finally mirror polished. After that, they were layered with CrAgN. The Ag-content in the layers was chosen to 3 wt% and 15 wt% respectively. Microstructural analysis revealed that the addition of 3 wt%Ag did not influence the growth manner of the films but the addition of 15 wt%Ag has made considerable changes in the film growth. The layer with 3 wt%Ag had excellent adhesion on the steel substrate. On the other hand, the addition of 15%Ag had strongly negative impact on the coating adhesion. Similar effect of different Ag addition has been established also to both the hardness and the Young modulus of the films, also. Both films have superior tribological properties against hard material (alumina) as well as against soft counterpart (CuSn6 as-cast bronze).

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1. Introduction

Thin CrN-based films have been used in variety of industrial applications like copper machining, aluminium die casting and forming and wood processing [1 - 7]. 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 was based upon the fact that commercially available lubricants (sulphides, oxides, graphite) exhibit considerable shortcomings and can not be used effectively in tooling applications. Soft noble metals, on the other hand, posse stable chemical behaviour and can exhibit self-lubricating properties due to their low shear strength.

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. These particles are stable up to high temperatures, have low hardness and shear strength and do not behave as abrasives. Silver containing transition metal nitrides films have been extensively studied in recent years. Various authors established that the addition of small amount of silver into ZrN, yttria stabilized zirconia and CrN increases the H^3/E^2 – ratio [8], wear resistance [9] and significantly reduces the friction coefficient [10 - 13].

CrAgN coatings deposited on various

substrates, but excepting ledeburitic tool steels, were studied by several authors [11 - 13]. They established alterations in the CrN-layer growth orientation with increased Ag-content [12]. The friction coefficient of the layers with 22 at.% Ag, measured for the 100Cr6-steel counterpart at 600 ^{o}C was reduced from 0.64 (pure CrN) to 0.47 (CrN+22 at.% Ag) [11]. As reported elsewhere [13], silver diffuses to the surface at high temperature, forms lubricious grains there, which gives the principal explanation of superior tribological properties of the CrAgN-films.

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 basic coating characteristics like wear resistance, friction coefficient, Young´s modulus, as a function of the silver content and deposition temperature.

2. Experimental

2.1. Material and processing

The experimental 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 procedure to the semi-final dimensions (plates 55 x 10 x 1 mm), they were subjected to standard heat treatment procedure. After that the samples were fine ground and polished with the diamond suspension up to the mirror finish.

The CrN- and CrN/Ag - 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: One made from pure chromium (99.9%Cr) and the second made from silver of 99.98% of purity). The cathode output power was 5.8 kW on the chromium cathode. On the silver cathode, the output powers were 0.1 and 0.45 kW in order to produce the silver contents in the coating of 3 wt% and 15 wt%, respectively. The processes were carried out in a low pressure atmosphere (0.15 mbar), containing the nitrogen and the 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 the deposition, the substrates were sputter cleaned in an argon low pressure atmosphere for 15 min. The substrate temperature was 250 ^{o}C for the cleaning. For the deposition, the temperature was increased to 500 ^{o}C using an internal wall heating. 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 hours.

2.2. Investigation methods

Microstructural analysis has been carried out on fracture surfaces of coated samples, on the field emission scanning electron microscope JEOL JSM-7600F. Coated specimens were immersed into liquid nitrogen and broken down before the analysis.

The nanohardness and the Young´s modulus (E) of the coatings were determined using the instrumented nanoindentation test under a normal load of 20 mN, at a NanoTest (Micro Materials Ltd) nanohardness tester equipped with a Berkovich indenter. For both coatings, ten measurements were made and the mean value and the standard deviation were calculated. The nanohardness and the Young´s modulus (E) of the coatings were determined using the instrumented nanoindentation test under a normal load of 20 mN, at a NanoTest (Micro Materials Ltd) nanohardness tester equipped with a Berkovich indenter. For both coatings, ten measurements were made and the mean value and the standard deviation were calculated.

The adhesion of the coatings on the substrate has been evaluated using a CSM Revetest scratch-tester. The scratches were made under progressive increasingly load from 1 N to 100 N, with a loading rate of 50 N/min. Standard Rockwell diamond indenter with a tip radius of 200 μm was used. Five measurements were made on each specimen and the mean value of adhesion, represented by the L_{c1} and L_{c2} critical loads, respectively, has been calculated. The critical loads were determined by the recording of the signal of acoustic emission as well as by the viewing of the scratches on the light micrographs. The L_{c1} critical load corresponded to the occurrence of first inhomogenities in the coating and the L_{c2} critical load was determined as load when 50% of the coating was removed from the substrate.

Tribological properties of the coatings were measured using the CSM Pin-on-disc tribometer, at ambient and elevated temperatures, up to 500 °C. For the testing, the balls with a 6 mm in diameter, made from sintered alumina and CuSn6 bronze have been used. No external lubricant was added during the measurements. The normal loading used for the investigations was 1 N. For each measurement, the number of cycles was 5100, e.g. at the sliding radius of 5 mm, the total sliding distance was 100 m.

3. Results and discussion

The microstructure of the substrate material after the heat treatment is in Fig. 1. The material consists of the matrix, formed with tempered martensite and fine carbides, uniformly distributed throughout the matrix.

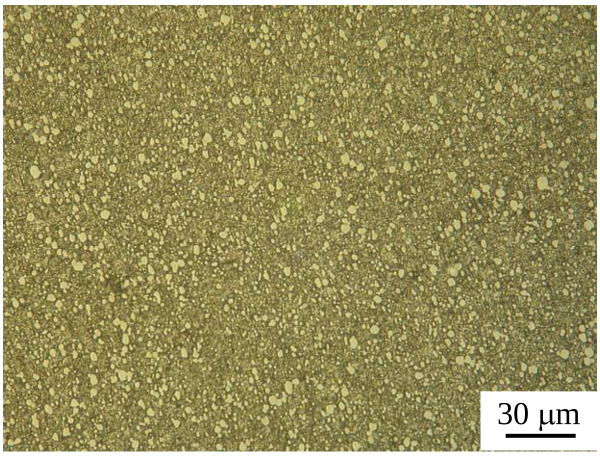

Fig. 1. Microstructure of PM ledeburitic steel Vanadis 6 substrate after heat treatment
(full colour version available online)

As established recently [14] that it is mainly the M_7C_3-phase that underwent the dissolution in the austenite during the heat processing. This results in the saturation of the austenite with carbon and alloying elements, which leads to high hardness of as-heat treated material. Other part of the M_7C_3-carbides, and almost complete amount of MC-phase remained undissolved. After the heat treatment, the average hardness of the material was 724 HV 10.

The thickness of the film with 3%Ag – addition was 4.2 μm, Fig 2a. Previous paper [16] was devoted to the analysis of CrAgN films prepared at a temperature of 260 °C (corresponding to heating up due to ion bombardment only). It has been established that the films formed at low temperature have a similar thickness, e.g. higher deposition temperature does not influence the growth rate significantly at a given Ag addition. On the other hand, the film with an addition of 15 wt% Ag has grown much faster and its total thickness was established to be 6.3 μm, Fig. 2b.

The film with 3 wt% Ag addition grew in a columnar manner, with well visible individual crystallites, Fig. 2a. There is no difference in a growth manner between this film and that formed at 260 °C, as reported previously [15]. The situation in the case of the film with an addition of 15 wt% Ag is clearly different – individual columnar crystals are not visible but separate Ag-particles can be shown on the SEM micrograph, Fig. 2b.

SEM micrograph in Fig 3a, made from the surface in the BE-detection regime, and corresponding EDS mapping of Ag, Fig 3b show that silver forms individual grains on the surface at higher concentration. Previous paper [15] did not documented this fact – mainly due to the fact that lower temperature was used for the deposition and the silver concentration was too low for the formation of individual crystals of sufficiently large size to be detected by SEM.

In the paper published previously [15] it was concluded that the addition of 3 wt%

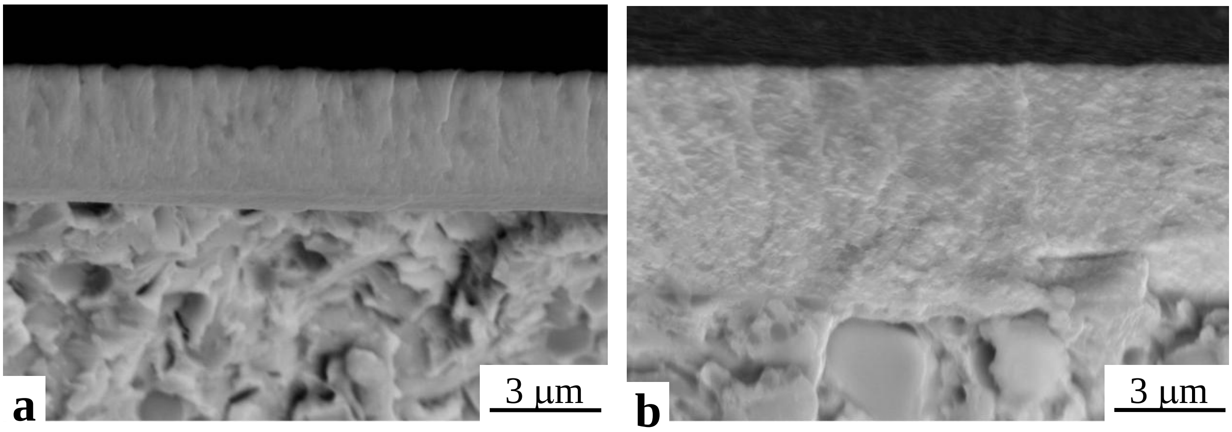

Fig 2. SEM micrographs showing: (a) the microstructure of CrAg3N and (b) CrAg15N films developed on the Vanadis 6 steel substrate

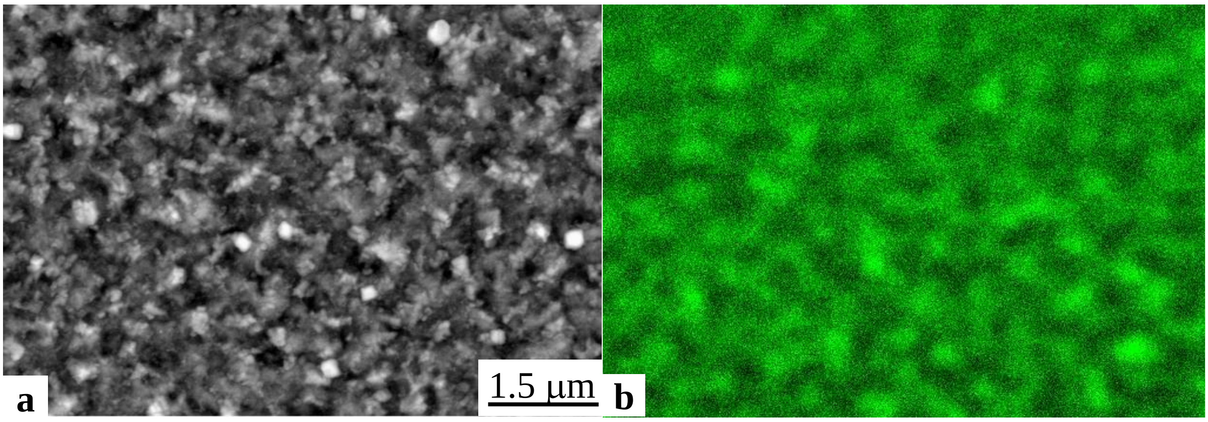

Fig. 3. SEM micrograph showing (a) the surface microstructure of CrAg15N – film and (b) corresponding EDS-map of silver

(full colour version available online)

Ag induced only very slight coating hardness decrease. The nanohardness of pure CrN was 16.79 ± 1.49 GPa and that of CrAg3N 15.97 ± 1.44 GPa. Current results confirmed that small Ag-addition does not result in significant changes in coating hardness – the hardness of 3 wt% Ag containing film deposited at 500 °C was 16.13 ± 1.83 GPa, Table 1. The addition of 15 wt%Ag, on the contrary, led to substantial hardness reduction – it was only 11.43 ± 0.61 GPa. Similar effect of the silver addition on the coating hardness has also been reported by Yao et al. [16] for magnetron sputtered nanocomposite coatings with various silver additions. An explanation can be given by the fact that Ag is very soft in nature and the Ag-particles embedded in CrN make a softening of the coating. Also the size of Ag-particles should be probably considered – the larger the Ag-grains are the more considerable softening of the film. The Young´s modulus of pure CrN and CrAg3N deposited at 260 °C were of about 240 GPa [15]. Also, small Ag addition in the film formed at 500 °C did not change the Young modulus, see also Table 1. But, higher silver amount incorporated into the basic CrN has a negative effect on E. The investigations published by Aouadi et al. [8], where decreased Young´s modulus with increased Ag-content in YSZ-based coatings has been established, has thus been confirmed.

For the film with 3 wt% Ag addition, the first symptoms of coating damage occurred at the average loading of around 47 N (L_{c1}). Coating damage begins with an appearance of

Table 1.

Mechanical properties of the layers deposited at 500 °C

Coating	Hardness [GPa]	Young´s modulus [GPa]
CrAg3N	16.13 ± 1.83	246 ± 17
CrAg15N	11.43 ± 0.61	204 ± 6

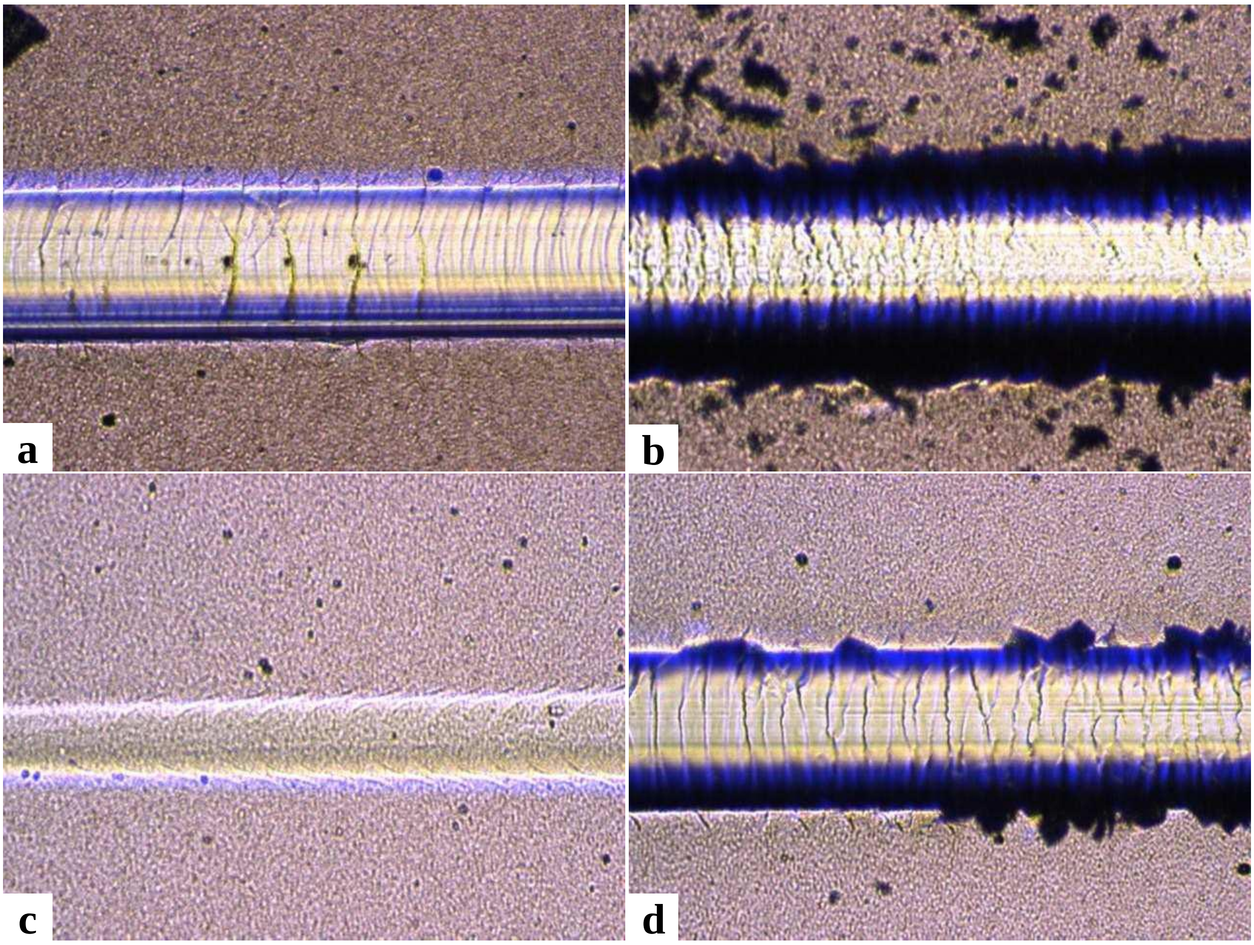

Fig. 4. Light micrographs showing the failures after scratch test: a – CrAg3N, L_{c1}, b – CrAg3N, L_{c2}, c – CrAg15N, L_{c1}, d – CrAg15N, L_{c2}

(full colour version available online)

semi-circular tensile cracks, Fig. 4a. The “total” failure of the CrAg3N - film is in Fig. 4b. It is typical by the occurrence of many parallel cracks in the scratch, where of about 50% of the coating is removed from the substrate. Typical load when this symptom occurred was 74 – 88 N (L_{c2}).

Relatively softer 15 wt% of Ag containing coating fails also by the manner of semi-circular tensile cracks, but the distance between the cracks is much larger than that in the CrAg3N-film, Fig. 4c. The critical load at which these symptoms firstly occurred was very low – it ranged around 6.4 N, Table 2. Figure 4d shows the total failure of the CrAg15N coating. Here, higher distance between adjacent cracks is also clearly evident. One can assume that softer CrAg15N - coating can store a higher amount of plastic energy before failure. This seems to be logical since silver is soft in nature, forms individual particles in the coating and can make the coating more resistant to the brittle failure.

Table 2.

Critical loads for defined degree of coatings failure

Coating	L_{c1} [N]	L_{c2} [N]
CrAg3N	46.9 ± 8.1	82.6 ± 8.4
CrAg15N	6.4 ± 0.6	44.1 ± 6.3

Table 3.

Friction coefficients of coatings against two different counterpart´s materials

Testing temperature [^{o}C]/coating	CrAg3N		CrAg15N	
	Al_2O_3	CuSn6	Al_2O_3	CuSn6
Room temperature	0.400	0.261	0.390	0.261
300	0.240	0.222	0.110	0.220
400	0.160	0.246	0.139	0.144
500	0.168	0.165	0.143	0.126

Total failure of the coating with the 15 wt% Ag addition became at much lower load than that of 3 wt% Ag containing film, Table 2.

Compared the obtained results to those recorded from the coatings developed at 260 ^{o}C it seems that elevated deposition temperature (500 ^{o}C) has favourable effect to the CrAg3N adhesion. For the coating with 15 wt% Ag, weak adhesion has been recorded. It seems that high silver content makes the coating too soft and very sensitive to the failure at higher loading.

Table 3 shows results of the measurements of friction coefficients. In all the cases, increased testing temperature led generally to decrease of the friction coefficient. At a room temperature, however, the friction coefficient against alumina was practically the same and, in addition, it does not exhibit any differences compared to pure CrN [15]. Therefore, our previous findings [15] were confirmed, e.g. no positive effect of the Ag-addition can be expected in low temperature applications. At higher operation temperature, on the contrary, there was positive effect of the silver addition found. This effect is slightly more evident for the 15 wt %Ag containing films.

The friction coefficient against bronze was lower for both coatings at a room temperature. There is, unfortunately, no direct comparison to the pure CrN available. At higher temperature, decrease of friction coefficient has been recorded, which is more significant for the film with higher Ag-content. Practical application of the coating with higher Ag-content is, however, doubtless. On the one side higher Ag-content induces an improvement of friction characteristics for both types of counterparts. On the other side, however, the film with high Ag-content had poor adhesion on the substrate. In addition, increasing Ag-content makes the film deposition process more expensive.

4. Conclusions

Investigations of magnetron sputtered CrN-films with various Ag-additions have brought the following findings:

The films with 3%Ag and 15%Ag formed at 500 ^{o}C had a thickness of 4.2 μm and 6.3 μm, respectively. Compared to the results obtained on the films developed at 260 ^{o}C it can be concluded that while the deposition temperature did not affect the final coating thickness, higher

Ag-content led to greater thickness of the film.

The CrAg3N-coatings grew in typical columnar manner. Addition of 15 wt% of silver induced substantial changes in the growth mechanism of the films. Moreover, individual silver grains became easily visible in the microstructure of the films.

The addition of 3 wt% of Ag into the CrN film did practically not influence the hardness. On the other hand, incorporation of 15 wt %Ag resulted in substantial hardness decrease and decrease of Young´s modulus.

The adhesion of CrAg3N-film formed at 500 ^{o}C was much better than that of the film with the same Ag-addition but made at 260 ^{o}C. The adhesion of the film with 15 wt% Ag was very poor.

Tribological measurements established excellent wear properties of both films at the temperatures above 400 ^{o}C. The friction coefficient was reduced by 70-75% compared to pure CrN.

From the point of view of the coating adhesion and, in addition, from the overall economy aspects it seems that the addition of 15 wt% of silver is too high and can not be recommended for the industrial use. On the other hand, the addition of 3 wt% Ag brings very promising benefits and its practical use should be investigated in the near future.

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