TRIBOLOGICAL PROPERTIES OF CrAgN THIN FILMS

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Resume

CrN and CrAgN thin films were magnetron sputtered onto the substrate made from Vanadis 6 cold work tool steel. The films were examined on tribological properties using a high temperature Pin-on-disc tribometer. Obtained results show that there is almost no effect of Ag addition on the friction coefficient when tested at a room temperature against alumina. The testing against the same counterpart at higher temperature gave positive effect of the silver addition on the friction coefficient. The testing against 100Cr6 ball bearing steel gave higher friction coefficient than that against alumina while the testing against CuSn6-bronze led to much lower µ. When tested at a room temperature, the wear performance of the films was positively affected only in the case of the CrAg3N film developed at 500 °C. On the other hand, addition of 3 wt% Ag into the CrN increased the wear performance at elevated temperatures while the addition of 15 wt% Ag has made the film too soft and sensitive to wear.

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1. Introduction

Chromium nitride thin films have generally good wear resistance [1, 2]. They can be synthesized in a wide range of chemistry, phase constitution and properties. Tribological properties of CrN-based films, however, cannot be changed in a sufficiently wide range since they are given by the nature of the film compound itself. The external lubrication brings one of possible way how to vary them, but, commercially available lubricants exhibit considerable shortcomings. Graphite and molybdenum disulfide, for instance, undergo oxidation above 300 °C and, hence, degrade rapidly. Metallic oxides, on the other hand, cannot be used at low temperatures since they exhibit an abrasive behavior.

Self-lubricating composite films (SLCF) can overcome problems with external lubrication. They combine hard wear resistant matrix with addition of soft lubricious phases. Silver is the most common noble metal used as an addition to the SLCF. It possess stable chemical behaviour and can exhibit self-lubricating properties due to its low shear strength. In addition it is known that silver is capable to migrate to the free surface providing lubrication above 300 °C.

Several investigations were focused on the transition metals (TM) nitride films (except CrN) with silver addition. These experiments arrived to various findings, which can be summarized as follows: Silver addition of 5-12 wt% increased the hardness, the H^3/E^2 – ratio and the wear resistance of ZrN [3]. Incorporation of 12 – 20 at% of Ag into yttria-stabilized zirconia (YSZ) coatings induced lowering of the friction coefficient, especially in the temperature range of 300 – 500 °C [4]. Above this temperature, the Ag- addition can not facilitate self-lubrication [4, 5]. In the case of magnetron sputtered vanadium nitride films, a large amount of silver atomic percent (42 % Ag) has been found to be needed to provide self-lubricating [6]. Silver addition can effectively relieve internal residual stresses in the films when exposed at a temperature of 380 °C and higher [7]. Finally, silver can increase the antimicrobial activity of the surface [8].

CrAgN coatings deposited on various substrates have been studied by several authors [9 - 12]. Silver is almost completely insoluble in CrN and forms nano-particles in CrN-matrix. Ag-addition in the CrN-layer changed the growth manner of the CrN-crystals [10, 13] and reduced the friction coefficient against 100Cr6 counterpart significantly [9]. There is a good consensus on the lowering of friction coefficient at temperatures 300 – 500 °C [4 - 6, 9]. On the other side, tribological properties differ significantly above 500 °C whereas the nature of the matrix is the key factor influencing their improvement [6] or deterioration [4, 5, 9]. One can assume that silver, as a naturally soft metal, should reduce both the hardness and the Young modulus of the films. But, some experimental works established either "no effect" of silver or slight increase of the hardness [14]. The information on the effect of silver on the adhesion of films is lacking – one of possible reason is that various materials with completely different properties were used as substrates. But, very good adhesion on the Vanadis 6 ledeburitic tool steel has been established in our recent work [15]. No negative effect of CrAgN on toughness of Cr-V ledeburitic tool steel has been established recently [13].

The choice of "optimal" silver addition into the basic film is not doubtless yet – many authors recommended the films with very high silver contents [4, 5, 9 - 12] although it seems that much lower Ag-addition can lead to superior tribological parameters, also [14].

2. Experiment

The CrN- and CrAgN - coatings were deposited onto coupons made from Cr-V ledeburitic steel Vanadis 6. Prior the deposition, the substrate material was heat treated to a hardness of 60 HRC, ground and polished up to the mirror finish. The deposition has been conducted 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 CrN, two targets from pure chromium (99.9 %Cr of purity) were used. The target output power was adjusted to 2.9 kW for each cathode. For the deposition of Ag containing films, one silver cathode (99.98% of purity) was inserted into the processing chamber instead of one Cr target. In these trials, 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 Ag contents in the coating of 3 wt% and 15 wt%, respectively. Two deposition temperatures have been used. The first one was 250 °C. To achieve that, the samples were heated using resistive heaters during the sputter cleaning step. Afterwards, the substrate temperature of 250 °C was kept constant by ion bombardment only. The second deposition temperature was 500 °C. It was achieved by resistive heaters placed on internal walls of the processing chamber. The processes were carried out in a low pressure atmosphere (0.15 mbar), containing pure nitrogen and argon (both of 99.999 % of purity), in a ratio of 1:4.5.

Specimens were ultrasonically degreased in acetone and loaded into the processing chamber. They 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 °C for the cleaning. 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.

The microstructure of substrate material as well as the coating characterization (microstructure, hardness, Young modulus, adhesion) was reported elsewhere [13, 15, 19].

Tribological properties of the coatings were measured using the CSM Pin-on-disc tribometer, at ambient and 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 at all the temperatures. The balls made from heat processed 100Cr6 ball bearing steel (hardness of 700 HV 10) were used, also, but for the testing at ambient temperature only. The experiments were conducted in laboratory air, at a relative humidity of 40 – 50 %. 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. the total sliding distance was 100 m at the sliding radius of 5 mm. After the testing, the wear tracks widths were measured on light microscope ZEISS NEOPHOT 32 at a magnification of 50x. Ten measurements were made on each track and the mean value, which was used for further evaluation, was calculated. The volume loss and wear ratio of coated samples were calculated from the width of the wear tracks using the formulas [16]:

$$V_l = 2\pi R\left[\frac{r^2}{\sin\left(\frac{d}{2r}\right)}\right] - \frac{d}{4}\sqrt{4r^2 - d^2} \qquad (1)$$

$$W = \frac{V_l}{l \times F_n} \qquad (2)$$

where *R* is the wear scare radius, *d* is the mean value of wear track width, *r* is the radius of the ball counterface, *l* is the sliding distance and F_n is the normal load applied.

3. Results and discussion

Fig. 1 gives an overview of the friction coefficients μ resulted from testing at a room temperature for all the used counterparts. The pure CrN film has the μ of 0.378 when tested against alumina. CrAg3N films grown at 250 and 500 °C had average friction coefficients of 0.389 and 0.373, respectively. The lowest average μ (0.365) against alumina was recorded for the 15 wt % Ag containing film. Generally, the testing against 100Cr6 ball bearing steel gave slightly higher μ compared to alumina. The pure CrN film had average μ of 0.425. The silver containing films had slightly lowered friction coefficient, e.g. around 0.4, but it should be noted that the friction coefficients values ranges overlap. These results indicate that almost no positive effect of Ag addition was found when alumina ball as well as 100Cr6 steel have been used as a counterbody.

Testing against CuSn6 bronze ball gave lower friction coefficient. The pure CrN film had a μ = 0.332. Silver addition of 3 wt % tended to lower friction coefficient and the lowering of friction coefficient became even more significant for the composite Ag-containing films grown at a temperature of 500 °C. The impact of silver incorporation into the basic CrN compound can be thus considered as slightly positive when tested against bronze at a room temperature.

Fig. 2 shows the friction coefficients μ recorded by testing against alumina at a room and elevated temperatures. As above stated, almost no difference in μ were found when tested at a room temperature. Testing at 300 °C, however, yields to different behaviour of the coatings. The friction coefficients for the pure CrN, CrAg3N grown at 250 °C, CrAg3N grown at 500 °C and CrAg15N formed at 500 °C were 0.357, 0.304, 0.238 and 0.110, respectively. Higher testing temperature lowered the difference in the μ for different coatings, for instance, the μ recorded by the testing at 400 °C were 0.256, 0.194, 0.160 and 0.139 for the pure CrN, CrAg3N formed at 250 °C, CrAg3N formed at 500 °C and CrAg15N formed at 500 °C, respectively. The measurement at 500 °C gave rather similar results.

Table 1 shows the wear ratios at ambient and elevated temperatures when alumina counterpart was used. At a room temperature, beneficial effect of silver addition is evident only in the case of the CrAg3N film grown at

500 °C. Compared to pure CrN, the wear ratio is lowered 2 times. For 3 wt% Ag containing film grown at 250 °C, slight worsening of wear ratio has been recorded and, for the 15 wt% Ag containing film the wear ratio is higher in an order of magnitude.

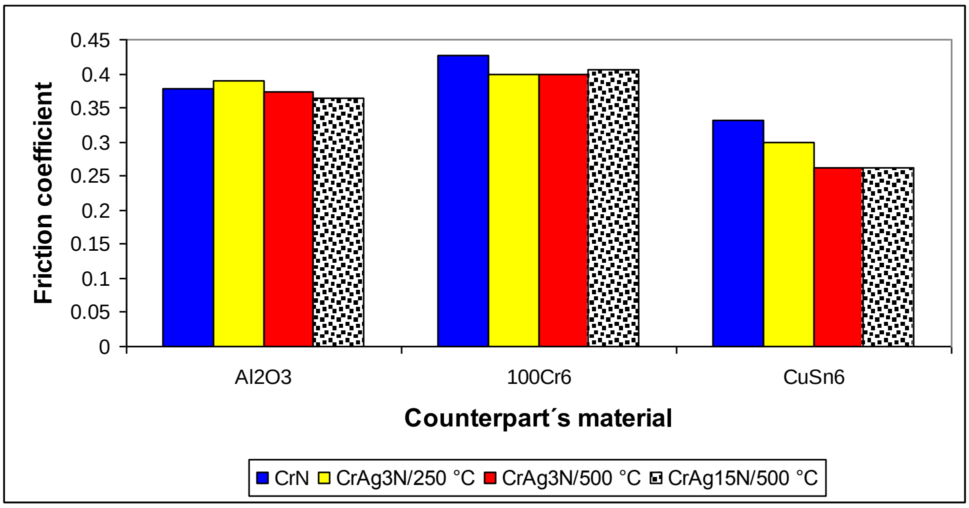


Fig. 1. Average friction coefficient of investigated films against various counterpart materials, testing at a room temperature, normal load applied of 1 N.
(full colour version available online)

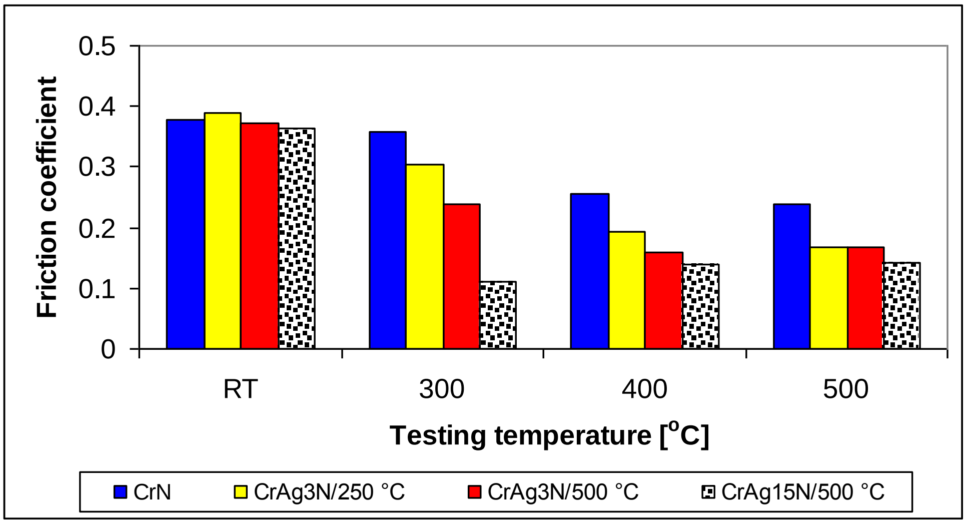


Fig.2. Average friction coefficient of investigated films against alumina at a room and elevated temperatures, normal load applied of 1 N.
(full colour version available online)

Table 1

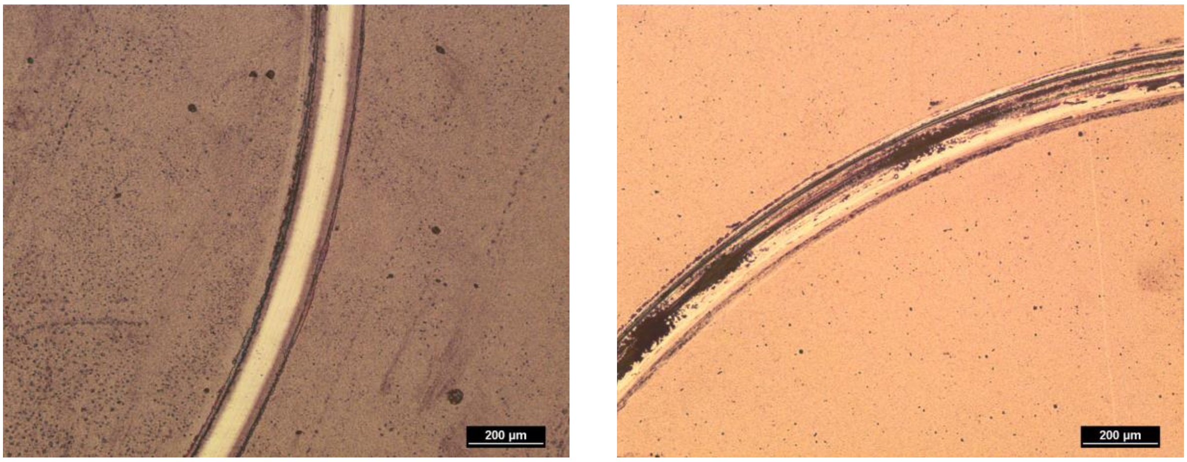
Wear ratio at ambient and elevated temperatures, alumina used as a counterpart

Testing temperature [°C] / coating	**CrN**	**CrAg3N/250 °C**	**CrAg3N/500 °C**	**CrAg15N/500 °C**
Room temperature	6.947×10^{-13}	7.399×10^{-13}	3.65×10^{-13}	1.031×10^{-12}
300	2.926×10^{-11}	2.894×10^{-11}	8.405×10^{-12}	7.053×10^{-12}
400	1.162×10^{-11}	4.329×10^{-12}	9.927×10^{-12}	1.925×10^{-11}
500	1.927×10^{-11}	6.208×10^{-12}	1.522×10^{-11}	4.802×10^{-11}

The testing at elevated temperature led to increase of the wear ratio for the CrN film. The film with 3 wt% Ag addition grown at 250 °C behaved in a very similar way from the qualitative point of view. The wear ratio was minimal after the testing at an ambient temperature, which was followed by steep increase at 300 °C and decrease at 400 and 500 °C, respectively. But, it is clearly evident that the wear ratios after the testing at these temperatures are considerably lower than that of CrN. The film with the same Ag content grown at 500 °C had lower wear ratios than that grown at 250 °C at the room temperatures and 300 °C, respectively. However, the testing at higher temperatures brought higher wear ratio. The film, which contains 15 wt% Ag had the lowest wear ratio when tested at 300 °C, but, the wear ratio increased as the testing temperature increased and, the increase of the wear ratio was found to be greater than those of other investigated films.

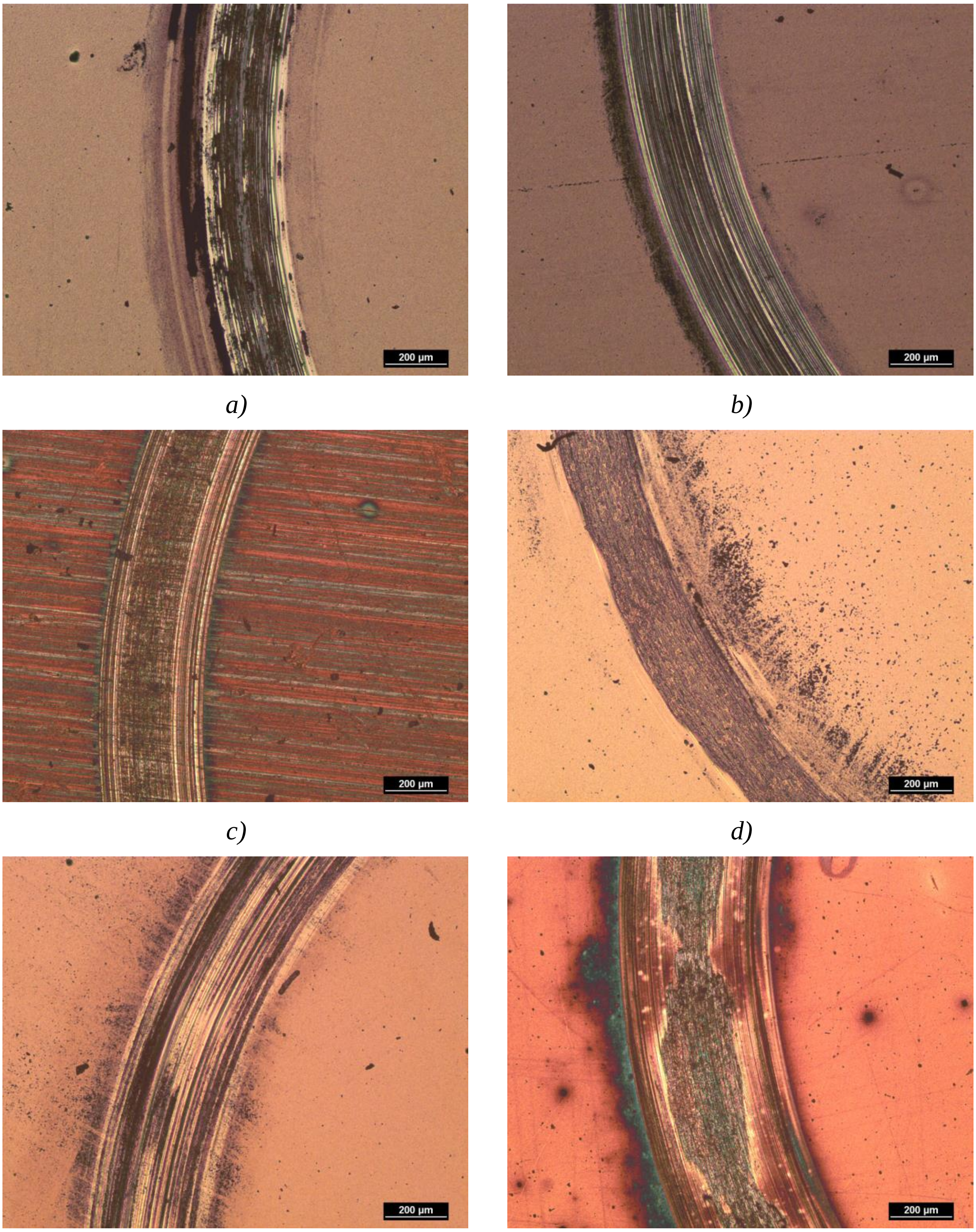
The results of wear ratio measurements at a room temperature are well consistent with the obtained values of friction coefficients – the wear ratios decreased with decrease in the μ. The only one exception is shown in the case of 15%Ag containing film – higher wear ratio of this film can be attributed to its softness.

In order to explain the temperature behaviour of the coatings, it should be noted that there was no lubricant added to the experimental setup. The fact that the wear ratio was lower or higher can thus be attributed only to the self-lubricating effect of the silver and to the effect of Ag on the film hardness. The self-lubricating effect is prevalent only above the testing temperature of 400 °C, when the Ag-atoms are capable of being transported to the surface. Below, but above an ambient temperature, only the effect of the softening of the coatings can be expected. It was reflected by much higher wear ratio at 300 °C than that at ambient temperature. Finally, it should be also noted that the softening of alumina could take place during the testing [17]. The behaviour of the film, which contains 15 wt% Ag can be characterized as a special case. Incorporation of 15 wt% Ag makes the film soft [15]. This gives a natural explanation of high wear ratio at ambient temperature. At a temperature of 300 °C, the friction coefficient of the coating became extremely low and thereby the wear ratio was lowered, also. Above this temperature, however, the softening of the coating can be expected, as reported for instance by Kostenbauer at al [7], which gives a principal explanation of high wear ratio measured at 400 °C and 500 °C, respectively.



a) *b)*

Fig. 3. Light micrographs showing the wear scares of a) CrAg3N-film grown at 500 ^{o}C, b) CrAg15N-film grown at 500 ^{o}C, after sliding at a room temperature, alumina used as a counterpart.
(full colour version available online)



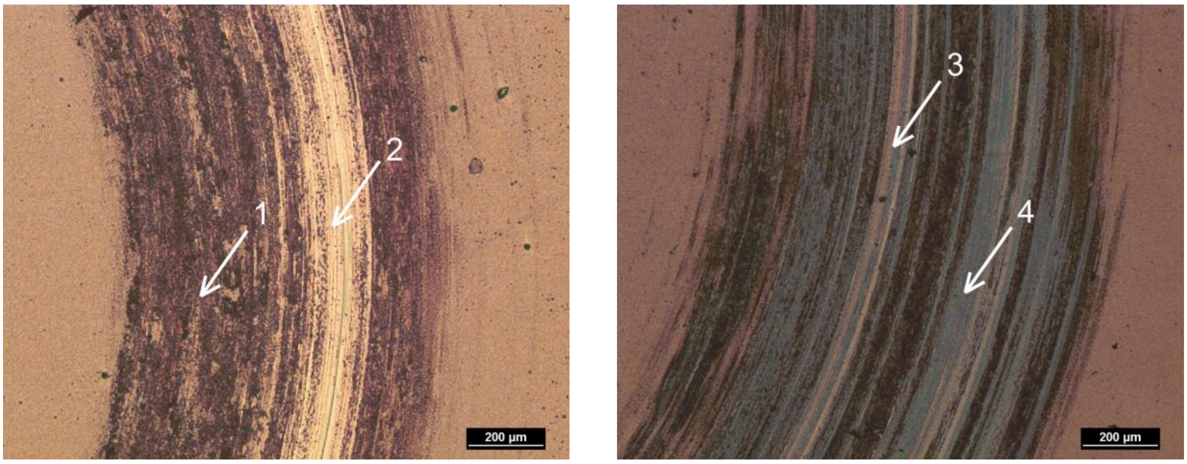
a) b)

c) d)

e) f)

Fig. 4. Plan view light micrographs showing the wear scares of CrAg3N-film grown at 500 °C, a) testing temperature of 300 °C, b) testing temperature of 400 °C, c) testing temperature of 500 °C, and CrAg15N-film grown at 500 °C, d) testing temperature of 300 °C, e) testing temperature of 400 °C, f) testing temperature of 500 °C

(full colour version available online)



a) *b)*

Fig. 5. Plan view light micrographs showing the wear scares of CrAg3N-film grown at 500 °C, after testing against CuSn6, a) room temperature, b) testing temperature of 400 °C
(full colour version available online)

The testing at 400 °C, Figs 4 b, e brought significant broadening of wear scares. This is highlighted for the CrAg15N film much more than that for CrAg3N, compare Fig. 4b and 4e. Here, the effect of softening of CrAg15N became prevalent and the self-lubrication by Ag – particles was insufficient to compensate the softening of the film. The testing at 500 °C highlighted the differences between tribological behaviour of the films containing 3wt% and 15 wt% Ag, respectively, Figs. 4c, f. The width of the wear track on the CrAg3N-film increased to 0.324 mm. Here, no symptoms of total failure of the film were observed. The width of the films, which contains 15 wt% Ag, was 0.477 mm. There are symptoms of total film failure clearly visible – free substrate surface is shown inside the wear scares.

Figure 5 shows representative plan view micrographs of the wear scares obtained by testing of CrAg3N-film, grown at 500 °C, against the CuSn6-ball. The testing at ambient temperature gave the wear tracks with a width of 0.89 mm, Fig. 5a.

There are two typical areas inside the wear scare. The first one can be classified as almost unaffected by the sliding of CuSn6-ball (1). The second part of the wear scare exhibits clearly visible symptoms of scraping (2). However, no evidence of counterpart´s adhesion has been recorded.

The testing at a temperature of 400°C produced the wear tracks with a width of 1.02 mm, Fig. 5b. Here, two typical areas inside the scare can be found, also. The first one is, similarly to the case of the testing at a room temperature, almost unaffected by the sliding (3). The dominant part of the wear scare, however, shows symptoms of considerable counterpart´s material transfer (4).

To explain the behaviour of the sliding couple CrAg3N deposited at 500 °C vs. CuSn6 bronze, various aspects should be considered. It should be noticed that the behaviour is determined by the fact that the CuSn6 is soft in nature (149 HV 10) and it has low shear strength, so that it can be easily smeared on the surface. This tendency is highlighted when higher testing temperature is used.

4. Conclusions

Tribological investigations of magnetron sputtered CrN-films with various Ag-additions arrived to the following conclusions:

- there is almost no effect of silver addition on the friction coefficient when tested at a room temperature against alumina but the testing against the same counterpart at higher temperature gave positive effect of the silver addition on the μ,

- the testing against 100Cr6 steel gave higher friction coefficient than that against alumina while the testing against CuSn6-bronze led to lower μ,
- when tested at a room temperature, the wear ratio was positively influenced only in the case of the CrAg3N film developed at 500 °C,
- addition of 3 wt% Ag into the CrN increased the wear performance at elevated temperatures while the addition of 15 wt% Ag has made the film too soft and sensitive to wear, which resulted in partial removal of the film from the substrate inside the wear scares.

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