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INTERACTION OF Cr_2N AND Cr_2N/Ag THIN FILMS WITH CuZn-BRASS COUNTERPART DURING BALL-ON-DISC TESTING

INTERAKCIJA Cr_2N IN Cr_2N/Ag TANKIH PLASTI V PARU S CuZn-MEDENINO MED PREIZKUSOM KROGLA NA DISK

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Cr_2N- and Cr_2N/Ag-nanocomposite thin films were deposited on a substrate made of Cr-V ledeburitic tool steel Vanadis 6 by reactive magnetron sputtering, at a deposition temperature of 500 °C, using pure Cr and Ag targets, in a composite, low-pressure N_2/Ar atmosphere. The additions of silver to the Cr_2N/Ag coatings were w = (3, 7, 11 and 15) %. Tribological testing using a ball-on-disc apparatus was realized at ambient temperature and, for the Cr_2N with the additions of mass fractions of Ag 7 % and 11 %, at the elevated temperatures of (300, 400 and 500) °C, respectively. Balls made of binary CuZn-brass (55 % Cu, 45 % Zn) were used as the counterparts. The wear tracks after the ball-on-disc testing and the worn balls were analyzed with scanning electron microscopy (SEM) and a microanalysis (EDX), and the wear rates were calculated. The adhesive wear was derived from a quantitative-point metallographic analysis. The obtained results infer that a considerable material transfer from the counterpart onto the surface of the coatings takes place during dry sliding. The material transfer (and the adhesive wear of the counterpart) is mainly due to the low shear strength of the brass used. Two main trends were observed. The first one shows that the adhesive material transfer decreases with the increasing silver content when tested at ambient temperature. The second trend indicates that the use of a higher testing temperature leads to a higher adhesive wear of the counterpart.

Keywords: Cr_2N/Ag-nanocomposite PVD coatings, ball-on-disc, adhesion, friction coefficient, wear rate

Cr_2N- in Cr_2N/Ag-nanokompozitne tanke plasti so bile nanesene na podlago iz Cr-V ledeburitnega orodnega jekla Vanadis 6 z reaktivnim nanašanjem z magnetronom pri temperaturi nanašanja 500 °C z uporabo tarč iz čistega Cr in Ag v kompozit v nizkotlačni atmosferi N_2/Ar. Dodatki srebra v nanose Cr_2N/Ag so bili w = (3, 7, 11 in 15) %. Tribološki preizkusi z uporabo naprave krogla na disk so bili izvršeni pri sobni temperaturi in pri Cr_2N tudi z masnim deležem dodatka 7 % in 11 % Ag pri povišanih temperaturah (300, 400 in 500) °C. Krogle, izdelane iz binarne CuZn-medenine (55 % Cu, 45 % Zn), so bile izbrane kot par. Sledovi obrabe po preizkusu krogla na disk in obrabljene krogle so bili analizirani z vrstično elektronsko mikroskopijo (SEM) in mikroanalizo (EDX), izračunane pa so bile tudi hitrosti obrabe. Adhezivna obraba je bila prikazana s kvantitativno točkasto metalografsko analizo. Dobljeni rezultati kažejo, da se med suhim drsenjem pojavi občuten prenos materiala iz krogle na površino nanosa. Prenos materiala (in adhezijska obraba krogle) je nastal večinoma zaradi majhne strižne trdnosti medenine. Opaženi sta bili dve glavni usmeritvi. Prva je bila, da se pri preizkušanju pri sobni temperaturi adhezivni prenos materiala zmanjšuje z naraščajočo vsebnostjo srebra. Druga pa, da uporaba višje temperature pri preizkusu povzroči večjo adhezivno obrabo krogle.

Ključne besede: Cr_2N/Ag-nanokompozitni PVD-nanosi, krogla na disk, adhezija, koeficient trenja, hitrost obrabe

1 INTRODUCTION

Hard ceramic coatings like CrN and TiN have been used for the last three decades due to their high hardness and chemical stability, high oxidation resistance and low wear rate[1,2]. They have gained great scientific interest and industrial popularity due to these properties in copper machining[3], alumina die casting and forming, and wood processing[4]. However, the friction coefficient of most transition-metal nitride coatings is fairly high (0.6–0.8) and the tribological effectiveness, especially at elevated temperatures, is insufficient[5,6]. Therefore, a lot of effort has been made in recent years to decrease the friction coefficient at room as well as elevated temperatures. Multi-functional coatings combining soft lubricating phases within a hard wear-resistance matrix offer good properties[7,8]. These coatings generally include one or more nanocrystalline phases in a functional matrix to provide improved mechanical and tribological properties and/or corrosion resistance. Some coatings are designed to be adaptive, that is, their properties follow the changes in the operating conditions. An example of an adaptive coating is a hard wear-resistance matrix with an incorporation of soft metals like Cu, Ag or Au. This method can improve the lubricating in specific tribological conditions[9]. Chromium nitrides combined with noble metals are relatively easy to co-deposit by reactive magnetron sputtering and they form nanocomposite structures due to a lack of miscibility between the matrix and the lubricant[10,11].

Silver is most commonly used as an addition to the TM-nitride thin films. It exhibits a stable chemical behaviour over a wide temperature range as well as in a variety of aggressive environments. Ag is capable to migrate to a free surface to form Ag particles providing lubrication above 300 °C and, thereby, distinctively reducing the friction coefficient[12].

Our recent investigations of the magnetron-sputtered Cr_2N-films with w = (3, 7, 11 and 15) % of silver amounts, deposited on the Cr-V ledeburitic steel Vanadis 6, can be summarized as follows[13–17]: the incorporation of silver in the Cr_2N matrix led to an improvement in the tribological properties at elevated temperatures, especially at 400 °C and 500 °C. Nevertheless, the addition of 15 % of Ag made the film too soft and sensitive to the wear, which resulted in a worsening of the tribological performance. On the other hand, the films with w = (7 and 11) % of Ag additions seem to be very promising.

In this paper, the tribological performance against a CuZn-brass counterpart of the nanocomposite coatings consisting of a hard Cr_2N matrix co-deposited with different Ag additions is investigated. The films were deposited onto the Cr-V ledeburitic steel Vanadis 6 using the magnetron-sputter technique.

2 EXPERIMENTAL WORK

The substrate material was the PM ledeburitic tool steel Vanadis 6 with mass fractions 2.1 % C, 1.0 % Si, 0.4 % Mn, 6.8 % Cr, 1.5 % Mo, 5.4 % V and Fe as the balance element.

The samples used for the investigation and the conditions for depositing Cr_2N- and Cr_2N/Ag- coatings were reported elsewhere[11]. In the case of the Cr_2N coatings, during the deposition, the power was 2.9 kW per cathode (both Cr). For the production of the Ag-containing coatings, the power of the Cr cathode was kept at 5.8 kW, while the power of the Ag cathode was varied (0.10, 0.21, 0.34 and 0.45) kW in order to prepare the films with different Ag concentrations (3, 7, 11 and 15) %.

The tribological properties of the coatings were measured using a CSM ball-on-disc tribometer at room temperature and, for the coatings with 7 % and 11 % of Ag, also at the elevated temperatures up to 500 °C. The balls of 6 mm in diameter, made from CuZn-brass (55 % Cu, 45 % Zn), were used for the tests. No external lubricant was added during the measurements. The normal load used for the investigation was 1 N and the total sliding distance for each measurement was 100 m. The volume losses V of the worn balls were calculated on the basis of the sketch shown on **Figure 1** using the following formula:

$$V = ((\pi \cdot h) \cdot (3\rho^2+h^2))/6 \qquad (1)$$

where R is the ball radius, h and ρ are the height and the radius of the worn spherical segment of the ball. Relating the volume loss to the normal load and sliding distance, the wear rates W were calculated.

After the testing, the wear tracks and the worn balls were examined with a scanning electron microscope (SEM) JEOL JSM-7600F and an energy dispersive X-ray analysis (EDX).

The adhesive wear was derived from the quantitative-point metallographic analysis carried out on the SEM micrographs of the tracks after the ball-on-disc testing.

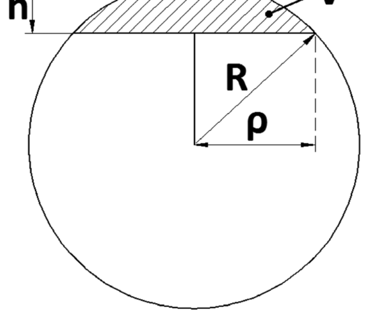

Figure 1: Sketch of a worn ball for the volume-loss calculation
Slika 1: Skica prikaza obrabe krogle za računanje volumenske izgube

3 RESULTS AND DISCUSSIONS

Figure 2 shows a detail of the track after the ball-on-disc test of the Cr_2N/11Ag coating tested at room temperature against the CuZn-brass counterpart. The surface of the coating did not show any indications of damage. On the other hand, thanks to the corresponding EDX maps, a considerable material transfer from the counterpart to the surface of the coating was detected; it was mainly due to the low shear strength of the brass used.

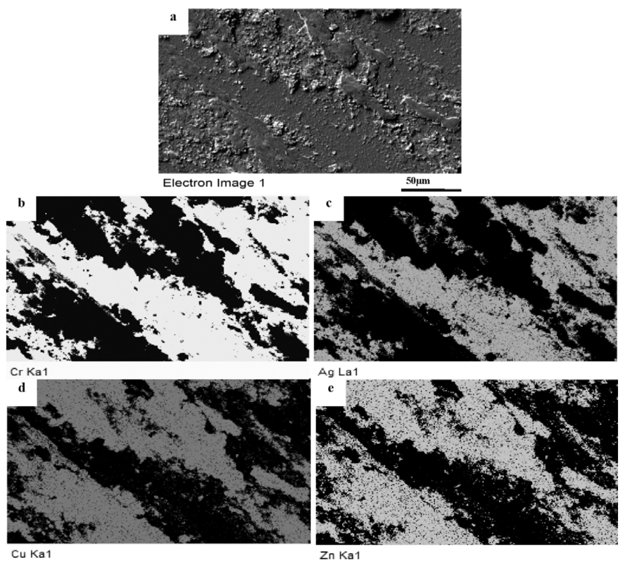

Figure 2: Transferred material of the CuZn-brass counterpart to the surface of the Cr_2N/11Ag coating after the ball-on-disc test at room temperature: a) overview, b) EDX of chromium, c) EDX of silver, d) EDX of copper, e) EDX of zinc
Slika 2: Prenesen material CuZn-medenine iz krogle na površino Cr_2N/11Ag-nanosa po preizkusu krogla na disk; preizkušeno pri sobni temperaturi: a) videz, b) EDX-kroma, c) EDX-srebra, d) EDX-bakra, e) EDX cinka

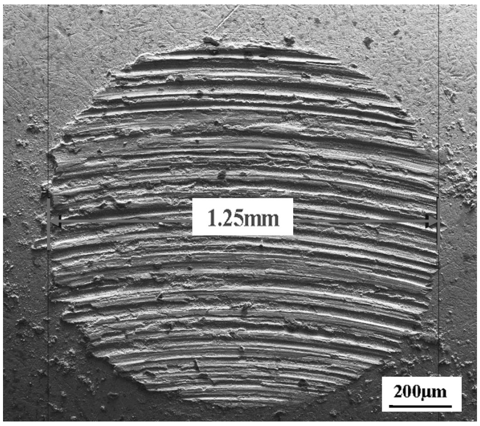

Figure 3: Worn CuZn-brass ball after the ball-on-disc test of the Cr_2N/11Ag coating at room temperature

Slika 3: Obrabljena krogla iz CuZn-medenine po preizkusu krogla na disku na Cr_2N/11Ag-nanosu, preizkušano pri sobni temperaturi

Figure 3 depicts the worn CuZn-brass ball after the ball-on-disc test of the Cr_2N/11Ag coating at room temperature. The parallel grooves oriented along the sliding direction are well visible and the diameter of the worn spherical segment is easily measurable. The surfaces of the worn balls were investigated with an EDX analysis to confirm the presence of silver. However, no signal of silver was obtained and one could assume that the silver content on the surface was too low to be detected with the EDX analysis.

The mean value of the friction coefficient examined at room temperature decreased with the increasing silver content in the Cr_2N matrix until 7 % (**Figure 4**). However, the influence of a higher silver content was not as positive for the friction coefficient as for the coating with 7 % Ag. The wear rates of the balls decreased by about 50 % for the coatings with the silver addition in comparison with the pure Cr_2N, and in the case of the coating with 15 % of Ag the decrease was about 75 % (**Figure 4**). These results were expected since silver can act as a solid lubricant, facilitating the sliding of the balls[12]. In our previous works[11,17] silver particles were well visible on the surface of the coatings after the deposition. On the other hand, the experiments carried out at the elevated temperature showed the opposite tendency. An increase in the testing temperature led to a slight increase in the mean value of the friction coefficient (**Figure 5**). As reported in the previous works[16,17], a decrease in the friction coefficient was observed with the increasing testing temperature, but there an alumina counterpart was used. In the case of the CuZn-brass counterpart the mechanism of the wear was different and a softening of the CuZn-brass alloy also took place at high temperatures.

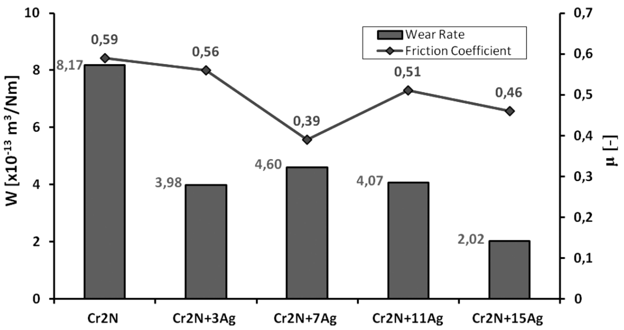

Figure 4: Wear rates W and friction coefficient μ of Cr_2N and Cr_2N/Ag coatings tested at room temperature

Slika 4: Hitrost obrabe W in koeficient trenja μ pri Cr_2N- in Cr_2N/Ag-prevlekah, preizkušanih pri sobni temperaturi

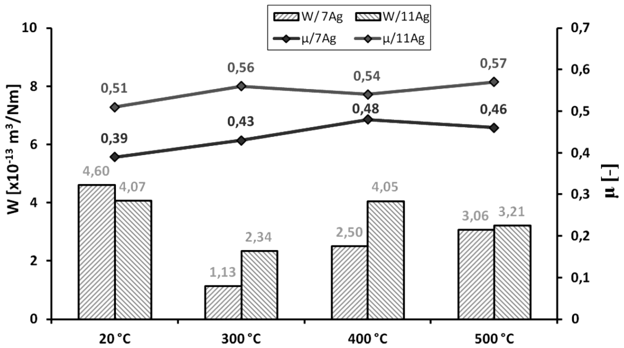

Figure 5: Wear rates W and friction coefficient μ of Cr_2N + 7Ag* and Cr_2N + 11Ag coatings tested at room and elevated temperatures, *previous result[16]

Slika 5: Hitrost obrabe W in koeficient trenja μ pri Cr_2N + 7Ag* in Cr_2N + 11Ag-nanosih, preizkušanih pri sobni in povišanih temperaturah, *predhodni rezultati[16]

Nevertheless, the wear rates of the CuZn-brass balls during the tribological testing of the coatings with mass fractions 7 % and 11 % of Ag at elevated temperatures were lower in comparison with the measurement at room temperature (**Figure 5**). The minimum values for both coatings were found at the temperature of 300 °C.

Figure 6 depicts the dependence of the friction coefficient on the sliding distance for the Cr_2N + 11Ag coating tested at ambient and elevated temperatures. All the measurements show a considerable instability. The friction coefficient is oscillating around the mean value in the range of 0.2. This can be explained with the cre-

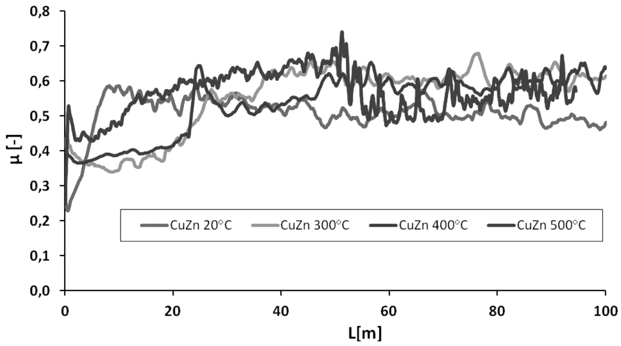

Figure 6: Dependence of friction coefficient μ on sliding distance L of the Cr_2N + 11Ag coating tested at different temperatures against the CuZn-brass counterpart

Slika 6: Odvisnost koeficienta trenja μ od dolžine drsenja L pri Cr_2N + 11Ag-nanosu, preizkušanem pri različnih temperaturah, v paru z CuZn-medeninasto kroglo

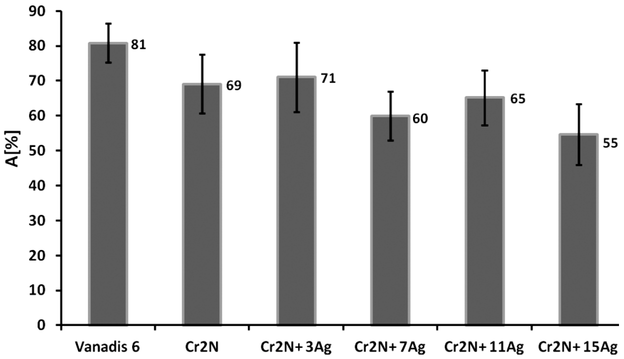

Figure 7: Area *A* of adhesion interactions between CuZn-brass and uncoated steel Vanadis 6, Cr_2N and Cr_2N/Ag coatings during ball-on-disc testing, at room temperature

Slika 7: Področje *A* adhezijske interakcije med CuZn-medenino in neprekritim jeklom Vanadis 6 ter Cr_2N- in Cr_2N/Ag-nanosi med preizkusom krogla na disk pri sobni temperaturi

ation of adhesion joins between the surface of the coating and the ball during the sliding and their subsequent release, accompanied with the oscillating of the friction coefficient.

A quantitative-point metallographic analysis was used to describe the adhesion interaction during the ball-on-disc testing. **Figure 7** shows the results of the testing at room temperature for the uncoated steel Vanadis 6, the pure Cr_2N and Cr_2N/Ag coatings. The highest adhesion wear was found for the uncoated substrate, where the area of adhesion interaction was $A = (81 \pm 5)$ %. For the coated substrate it is clearly evident that the adhesion wear decreases with the increasing silver content; the minimum $A = (55 \pm 8)$ % was found for the Cr_2N coating with the highest silver addition of 15 %. One can assume that the incorporation of silver into the Cr_2N matrix improves the wear of the CuZn-brass ball front view and also the area of adhesion interaction at room temperature.

On the other hand, the material transfer is more remarkable in the conditions of higher testing temperatures

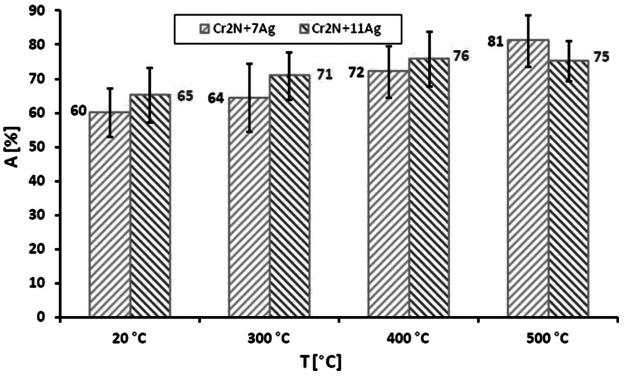

Figure 8: Area *A* of adhesion interactions between CuZn-brass and Cr_2N coatings with mass fractions of Ag 7 % and 11 % during the ball-on-disc testing at different temperatures

Slika 8: Področje *A* adhezijske interakcije med CuZn-medenino in Cr_2N-nanosi z masnim deležem Ag 7 % in 11 % med preizkusi krogla na disk pri različnih temperaturah

(**Figure 8**). Both coatings, Cr_2N with mass fractions of Ag w = (7 and 11) %, showed the same tendency, although the coating with 11 % of Ag exhibited a slower increase in the adhesion wear with the increasing testing temperature than the coating with 7 % of Ag. Most likely, the higher adhesion interaction at higher temperatures is caused by the softening of the CuZn-brass material, when the atoms of the ball material easily create the adhesion joins.

4 CONCLUSIONS

The friction and wear characteristics of the Cr_2N and Cr_2N/Ag coatings prepared with the magnetron-sputter-deposition method were investigated at room temperature and elevated temperatures during a ball-on-disc testing against a CuZn-brass counterpart. The results can be summarized as follows:

- During the tribological testing, a considerable material transfer from the CuZn-brass counterpart to the surfaces of all the tested coatings was observed.
- For the Cr_2N/Ag coatings, a lower friction coefficient and also lower wear rates of the balls were found during the testing at room temperature in comparison with the pure Cr_2N. This phenomenon is attributed to the silver incorporated into the Cr_2N matrix.
- Higher testing temperatures led to a slight increase in the friction coefficient. On the other hand, the wear rates of the balls were further decreasing, with the minimum values at 300 °C.
- During the testing at room temperature, the highest material transfer was found for the uncoated steel Vanadis 6. The adhesion wear was lower when the Cr_2N coating was tested. The decrease is more remarkable with the increasing silver content incorporated into the Cr_2N matrix.
- Higher testing temperatures led to increased adhesion interaction of both Cr_2N coatings, with mass fractions of Ag 7 % and 11 %.

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