

Nanocomposite Cr₂N-Ag thin films for tribological applications at elevated temperatures

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Cr₂N films with different silver additions (3-15 wt.%) were deposited on Vanadis 6 steel substrates using reactive magnetron sputtering, at a temperature of 500 °C. The obtained nanocomposite films are composed of the Cr₂N matrix with embedded metallic Ag particles. These particles are located on the crystal boundaries and their size is mostly up to 35 nm. The films grow in a typical columnar manner and have a thickness from the range 3.7 - 5.1 μm. The Ag addition (up to 11 wt.%) slightly increases the film hardness, its Young's modulus and adhesion to the substrate. The friction coefficient decreases rapidly with increasing the testing temperature. This is also reflected in generally lowered wear rate, as compared with Ag-free Cr₂N film. The 15 wt.% Ag addition, on the contrary, induces decrease in mechanical properties of the films, their lower adhesion on the substrate, and weaker tribological performance. Lower friction coefficient at elevated temperatures is attributed to silver migration to the free surface providing the films self-lubrication. An optimal temperature where the self-lubricating affect is most active is around 400 °C. A common practical recommendation can be derived based on the obtained results. If the goal is to get the best mechanical properties (nanohardness, Young's modulus) then the addition of 11 wt. % Ag into the Cr₂N is recommended. Alternatively, the Cr₂N-7Ag films can be designed for specific operation conditions where excellent tribological properties are required.

KEYWORDS: AG-CONTAINING FILMS, MICROSTRUCTURE, NANOHardNESS, ADHESION, TRIBOLOGICAL PERFORMANCE

INTRODUCTION

Magnetron-sputtered nanocomposite ceramic films with silver additions have attracted a great attention due to their wide range of applications. The addition of Ag expands the already existing properties of the films, providing them multiple "extra" characteristics such as antibacterial effects [1] wear resistance [2, 3, 4], self-lubrication properties at elevated temperatures, corrosion resistance [5] and light absorption enhancement [6].

Silver does not form carbides or nitrides and is in the metallic state in film. The mechanical properties of these films are mainly determined by their microstructure. Since the silver is insoluble in ceramics, only the microstructural changes due to Ag incorporation are responsible for modifying the mechanical properties. In general, an increase in silver produces a reduction of the hardness and Young's modulus of the films [7, 8]. But an opposite tendency was recorded for low silver contents since the Ag addition induces the grain refinement of the films [4, 8]. This refinement lowers the dislocation motion rate and may also prevent crack development inside the films.

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Conversely, more Ag segregates at the crystal boundaries at higher Ag contents incorporated into the matrix, thus enhancing the ductility, reducing the internal stresses and consequent hardness decrease.

In industrial applications, the combination of a hard ceramic film's matrix and silver as a solid lubricant is one of the main purposes of depositing Ag-containing films. The self-lubricating properties of these films are apparent mainly at elevated temperatures, due to the migration of Ag to the surface [7, 8, 9, 10, 11]. The silver amount and its distribution on the surfaces are dependent on the silver content in the films. More extensive silver migration is usually achieved by increasing the Ag-content [12].

The driving force of the mobility of silver atoms is a result of synergy of several sources: (i) chemical potential of Ag-particles [10, 11], (ii) concentration differences between the film's bulk and its surface, (iii) stress state of the film, and (iv) thermal energy (this is of why the silver transport is more active at elevated temperatures). Since the most common morphology of Cr_xN_y is columnar, the Ag-atoms diffuse along the column boundaries that act as diffusion channels [3, 6].

In most cases, the Cr_xN_y films are used in dry conditions. Under these conditions, the silver diffusion/migration to the surface is the key parameter controlling the self-lubricating features of film. Silver has very low shear strength. When forming islands at the surface it is capable to act as a lubricant during sliding against various counterbodies, especially at elevated temperatures [4, 13]. The result is, among others, the reduction of the friction coefficient (FC). Even at room temperature testing, reduction of the FC has been reported for larger Ag contents compared to the FC of pure Cr_xN_y [3, 4].

The opinions on the effect of Ag addition on the wear rate are inconsistent to date. In some works, a reduction of the wear rate of Cr_xN_y -Ag films (as compared with pure Cr_xN_y) was reported [3, 13] while increased wear rate [2, 4] was determined in others. Of note, the functionality of silver as a solid lubricant depends on certain conditions. First, silver must migrate to the free surface of the films. Second, the wear rate depends on the Ag depletion time because, after silver reservoir in the films is exhausted, a more unstable porous structure underneath the surface is created, causing film's failure [2]. Therefore, an equilibrium among the Ag content, silver mobility and the stability of the matrix must be reached to be able to exploit these self-assembled silver nanoparticles in a self-lubricating system.

MATERIALS AND METHODS

The substrate material was the Vanadis 6 steel (heat-treated to 60 ± 0.5 HRC) 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. The films were deposited by magnetron sputtering, in a pulse regime with a frequency of 40 kHz. Just prior to the deposition, the substrates were sputter cleaned in an argon low-pressure atmosphere for 15 min. 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. In the case of the Cr_2N film, during the deposition, the power was 2.9 kW per cathode (both Cr). To produce the Ag-containing films, 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) wt.%. The processes were carried out in a low pressure atmosphere (0.15 mbar), containing nitrogen and argon in a ratio of 1:4.5, at a deposition temperature of 500 °C.

Typical microstructures were obtained by investigations using a scanning electron microscope (SEM) coupled with energy-dispersive spectroscopy (EDS). The phase constitution of nanocomposite films was determined by X-ray diffraction. The nanohardness and the Young's modulus (E) values were measured using the instrumented nanoindentation test under a normal load of 60 mN using a Berkovich indenter. The penetration depth (and the loading) was chosen to not exceed one tenth of the film thickness, to minimize the substrate effect. The adhesion has been 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. Standard Rockwell diamond indenter with a tip radius of 200 μ m was used. Five measurements have been made and the mean value and standard deviation of adhesion properties, represented by the critical load when the first side delamination of the film occurred. Tribological properties were measured using the CSM Pin-on-disc tribometer at ambient and elevated temperatures, up to 500 oC. Balls 6 mm in diameter, made of sintered alumina were used for tests. No external lubricant was added during the measurements. The normal loading F used for the investigations was 1 N. For each measurement, the total sliding distance L was 100 m. The volume loss of coated samples was calculated by using the ASTM G99-17 procedure [14].

RESULTS

SEM images in Fig. 1 show cross-sectional microstructures of the obtained films. At 3 wt.% Ag addition the silver particles are almost invisible on the image, Fig. 1a. The total film thickness is 3.7 μm . In contrast, individual silver particles are well visible at 7 and 11 wt.% Ag addition, due to much higher backscattered electron yield of silver as compared with the film's matrix, Figs. 1b, c. The total

thickness of these two films is 4.3 μm . However, the silver particles in 15 wt.% Ag film appear in completely different way. As seen in Fig. 1d, silver forms lamellae that are oriented longitudinally to the surface, and have few hundreds of nm in length and less than 50 nm in width. Also it is seen that higher Ag addition fosters the film growth rate. The thickness of 15 wt.% Ag film is 5.1 μm .

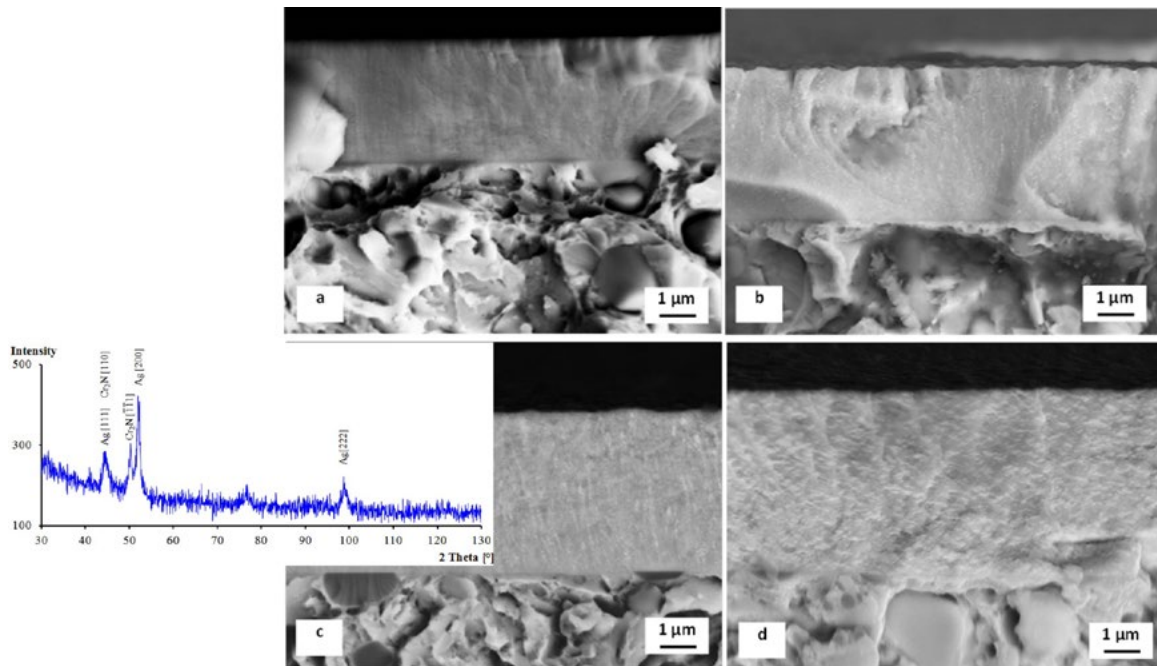


Fig.1 - Backscattered SEM micrographs of $\text{Cr}_2\text{N-Ag}$ films with: a) 3 wt.% Ag, b) 7 wt.% Ag, c) 11 wt.% Ag, and d) 15 wt.% Ag. X-ray diffraction patterns of 11 wt.% Ag film.

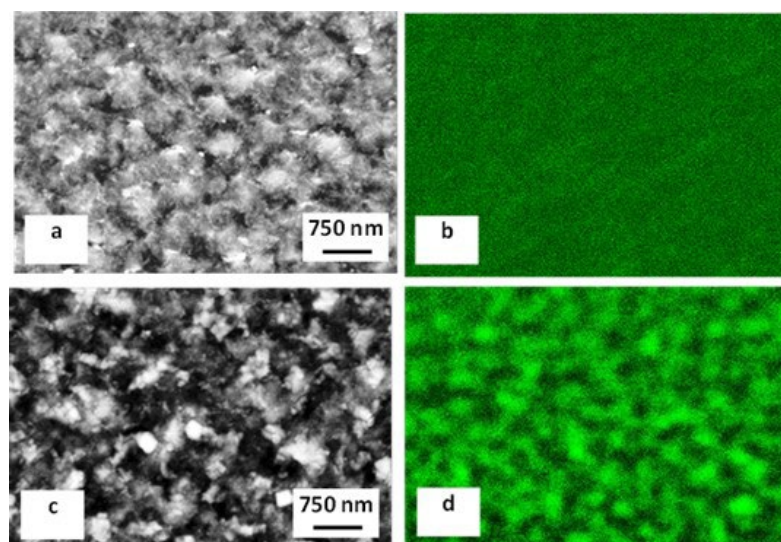


Fig.2 - Plan view SEM micrographs of $\text{Cr}_2\text{N-Ag}$ films with: a) 7 wt.% Ag, b) corresponding EDS map of silver, c) 15 wt.% Ag, d) corresponding EDS map of silver.

The Ag-particles are located mainly at the crystal boundaries, Fig. 2a,c. Their size is far below 50 nm in the case of 7 wt.%Ag film, but it may increase to several hundred nm for 15 wt.% Ag film. In this case the Ag is well visible on corresponding EDS map, Fig. 2d.

The nanohardness of Ag-free Cr₂N film is 16.8 ± 1.5 GPa, Fig. 3a. As seen in the diagram, the Ag additions up to 11 wt.% affect the nanohardness only slightly while 15 wt.% Ag reduces this property to 11.4 ± 0.6 GPa. The Young modulus (E) of pure Cr₂N is 244 ± 15 GPa, Fig. 3b. The Ag-addition leads to "almost no effect" on the E (at 3 or 7 wt.%), slight increase (11 wt.%) or rapid decrease (15

wt.%). The nanohardness measurements results are in good agreement with the literature [15]. It is stated that an increase in silver produces generally a reduction of the hardness and Young's modulus of the films. However, it was also found that the hardness can increase at low Ag contents, due to the grain refinement of the films. According to the data from [15] the maximum silver content leading to hardness increase is up to 15 at.%. On the other hand, the data on the effect of Ag on the E are inconsistent to date. One can only hypothesise based on the results reported in [16], that when the silver is added, the film is densified, and thereby makes it stiffer.

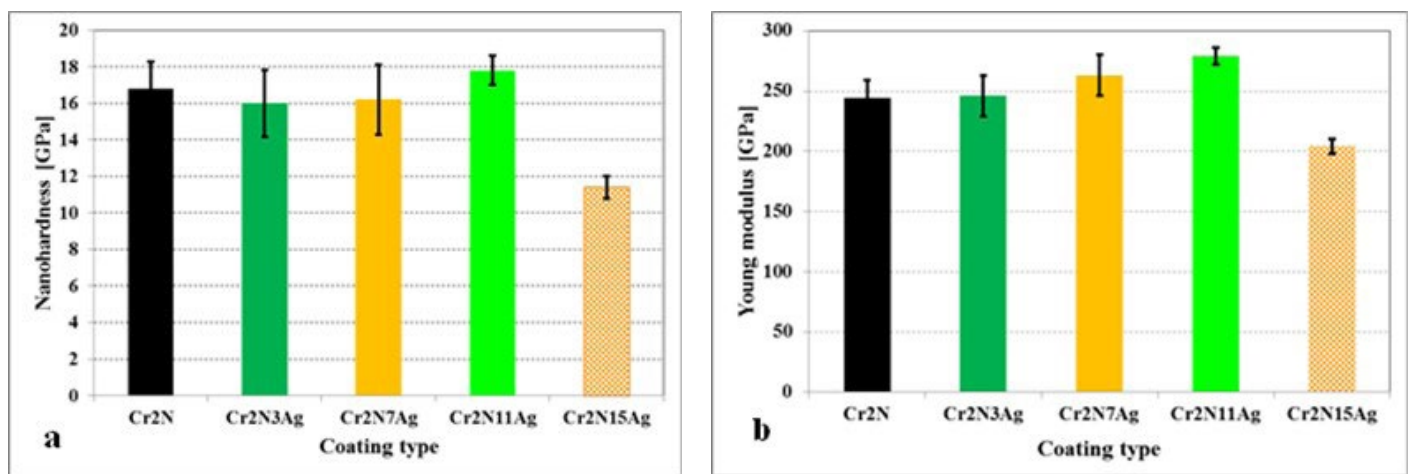


Fig.3 - Mechanical properties of Cr₂N-Ag films with different Ag contents. Cr₂N without a silver addition is a reference: a) nanohardness, b) Young's modulus.

The adhesion of films is improved by adding low silver amounts, Fig. 4. This may be due to the reduction of internal stresses within the films, owing to plastic deformation of silver particles. But, this effect is suppressed at higher

silver additions. The film becomes softer and thereby less resistant to the application of normal load during the scratch test. At this place it should be noted that, for instance, Yao et al. [17] arrived in very similar findings.

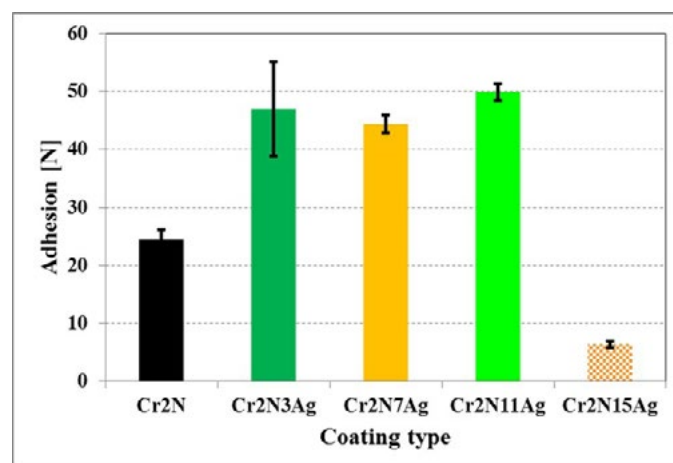


Fig.4 - Adhesion of Cr₂N-Ag films with different Ag contents. Pure Cr₂N is a reference.

The effect of silver addition on the friction coefficient is minimal at 20 °C, Fig. 5. However, significant reduction of FC was recorded at higher temperatures. When tested at

300 °C, the lowest FC had the film with 15 %Ag addition, but the situation was changed in favour of 7 wt.%Ag containing films in the case of testing at 400 or 500°C.

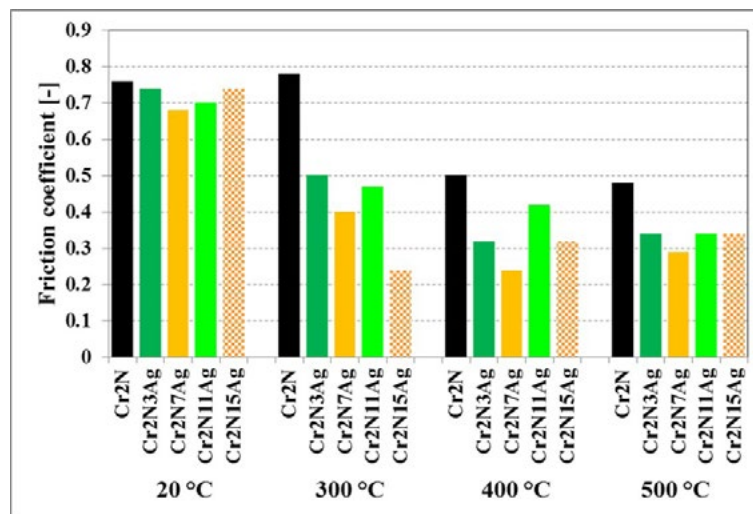


Fig.5 - Average (steady state) friction coefficient of Cr₂N-Ag films with different Ag contents, measured at different testing temperatures. Cr₂N without a silver addition is a reference.

The silver addition affects the wear rate only slightly during testing at 20 °C, except the 15 wt.% Ag film, Fig. 6. 15 wt.% Ag addition gives higher wear rate because of significant softening of the film. No effect of 3 wt.% Ag addition on the wear rate has been recorded at testing temperature of 300 °C, probably due to insufficient Ag content enabling the migration of Ag atoms to the free surface [12]. Increased

wear rate of 15 wt.% Ag containing film (not only at 300, but also at 400 and 500 °C), in the other hand, is a result of extensive softening of the film due to very high silver content. The 7 and 11 wt.% Ag gave very promising results with respect to the wear rate, when tested at 300 – 500 °C. However, at either 400 or 500 °C, also the 3 wt.% Ag works well.

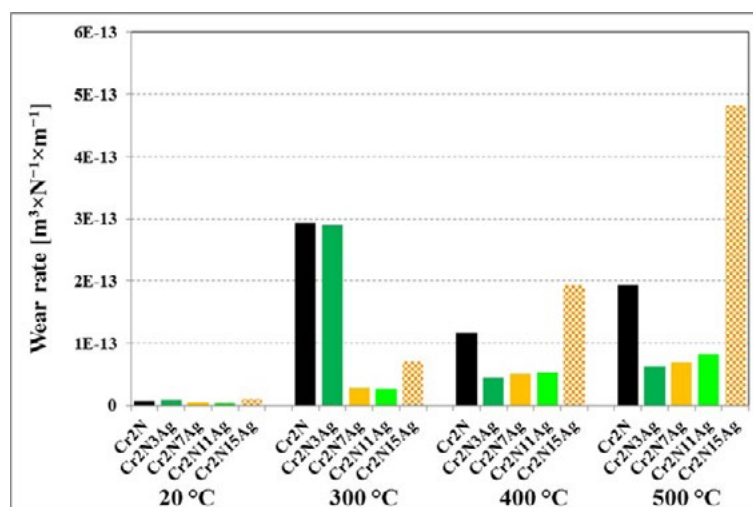


Fig.6 - Wear rate of Cr₂N-Ag films with different Ag contents, measured at different testing temperatures. Cr₂N without a silver addition is a reference.

CONCLUSIONS

Cr₂N films with 3-15 wt.% Ag additions were synthesised on Vanadis 6 steel substrates using reactive magnetron sputtering. The microstructure, nanohardness, Young's modulus, adhesion and tribological characteristics were investigated. The main outcomes of the experiments are the following:

The microstructures of films consisted of Cr₂N matrix with embedded Ag particles, mainly on the crystal boundaries.

The Ag additions up to 11 wt.% have slightly positive effect on the nanohardness, Young's modulus and adhesion of the films to the substrate.

The Ag-containing film manifest self-lubricating behaviour at elevated temperatures, which was demonstrated by

more than one half reduced friction coefficient.

The wear rate is considerably reduced for 7-11% containing films at all testing temperatures.

The 15%Ag addition reduced the mechanical properties of the films, which resulted in worsening of the wear performance despite superior reduction of friction coefficient.

Therefore, an addition of 7-11 %Ag additions can be recommended to obtain the best mechanical properties along with tribological performance of the films.

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