

Ag TRANSPORT IN Cr₂N_{0.62}-11Ag NANOCOMPOSITE COATING DUE TO THERMAL AFFECTION

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Abstract

Cr₂N_{0.62}-11Ag nanocomposite coatings containing 11 wt.% of Ag solid lubricant were deposited on substrates made of Cr-V ledeburitic tool steel Vanadis 6 by reactive magnetron sputtering at a deposition temperature of 500 °C. The experiments consisted of long term annealing up to 24 h at temperatures of 300, 400 and 500 °C, respectively, in closed-air atmosphere. The structural changes after annealing were evaluated by Auger electron spectroscopy (AES) and scanning electron microscopy (SEM). As a result of silver diffusion, the highest population density of silver particles on coating surfaces has been detected after 0.5 h and 4 h annealing at temperatures of 400 °C and 300 °C, respectively. Beyond the maximum peak, the population density of silver particles decreased with increasing the annealing time. Moreover, during annealing at temperature of 500 °C, very low population density was observed through all annealing process. This phenomenon was explained by sublimation of very small silver particles (less than 20 nm) and also by oxidation of coating surface, which was detected mostly during annealing at 500 °C. The oxide layer seems to be effective as a barrier of silver diffusion. The annealing of the films at temperatures below the deposition temperature induced limited both silver diffusion and depletion of silver within coating matrix.

Keywords: Chromium nitride, silver, magnetron sputtering, annealing, auger electron spectroscopy.

1. INTRODUCTION

In recent years, design or formulation of hard coatings with self-lubricating properties has become great popularity in scientific community as promising tribological coatings. In particular, the production of new coatings architectures based on nano-composite or -layered morphologies have become very popular [1].

Silver is the most commonly used element as an addition into the transition metal nitrides coatings. Studies on Ag-containing coatings deposited on various substrates have shown that elevated temperatures lead to Ag diffusion to the surface, yielding a lubricious bearing layer and it subsequently leads to the lowering of the friction coefficient at elevated operating temperatures in the range 300 - 500 °C [2-7]. On the other hand, the tribological performance of Ag-containing films undergoes worsening above 500 °C, since silver is less effective in providing lubrication while loaded because of excessive softening [8] and also the oxidic degradation of Cr-N/Ag here takes a part [9].

Silver is driven to the surface by a strong reduction in surface energy which occurs via transport from the metal nano-inclusions confined inside the composite matrix to the free surface of the material [10]. Diffusivity of silver is naturally dependent on silver concentration, temperature and also on the microstructure of the medium through which it diffused [5, 11, 12]. The diffusion of silver throughout the coatings brings also some drawbacks. After the noble metal transport to the surface, the coating becomes depleted in the lubricious metal and cannot act as a self-lubricated composite for long. Control of such diffusion process is, hence, needed for an extended lubrication.

Our recent results pertaining to the investigations of magnetron sputtered Cr₂N-films with the additions of 7 and 11 wt.% of Ag deposited on the Cr-V ledeburitic steel Vanadis 6 can be summarized as follows [3, 13, 14,

15]: the dominant phases in nanocomposite coatings are Cr₂N and Ag, and no phase changes were found after annealing at temperatures of 300, 400 and 500 °C, respectively, with a duration of 0.5 h. On the other hand, the friction coefficient of Cr₂N-Ag films decreased with increasing testing temperature rapidly when alumina ball has been used as a counterpart, with the minimum at temperatures of 400 and 500 °C, respectively, for both the coating with 7 and that with 11 wt.% Ag, also.

In this paper, we focused on the Ag transport within a Cr₂N matrix during annealing. The Cr₂N with 11 wt.% of Ag (cca. 4.7 at.%) nanocomposite coatings were deposited onto the Cr-V ledeburitic steel Vanadis 6 at temperature T_s = 500 °C and subsequently annealed up to 24 h at temperatures of T_a = 300, 400 and 500 °C. The presented results are a part of a comprehensive research.

2. EXPERIMENTAL

The substrate material was the powder metallurgical ledeburitic steel Vanadis 6 with nominally mass fraction: w(C) 2.1 %, w(Si) 1.0 %, w(Mn) 0.4 %, w(Cr) 6.8 %, w(Mo) 1.5 %, w(V) 5.4 % and Fe as a balance. The preparation of samples used for the investigation and the conditions for deposition of the Cr₂N/Ag nanocomposite coatings can be found in [14], for instance.

Coated samples were isothermally annealed to investigate the silver migration to the surface. Annealing of coated samples has been completed in a conventional multi-purpose chamber furnace in closed-air atmosphere at temperature 300, 400 and 500 °C, respectively, for a time of 0.5, 1, 2, 4, 8, 16 and 24 h.

Quantitative analysis of silver agglomerates on the surface, depending on the temperature and time of annealing, has been carried out on the SEM micrographs recorded at a magnification of 20 000x, in a regime of the detection of backscattered electrons (BE). At least forty micrographs have been used for the analysis after each annealing regime and the average values and standard deviations of the population density of Ag agglomerates [μm⁻²] were calculated.

The Ag concentration as a function of depth was determined by completing Auger electron spectroscopy depth profiles in a VG Microlab 310F for as-deposited (AD) and annealed films. Auger spectra were taken between each sputter etching step with the sputter gun turned off. The AES depth profiles were carried out just up to 1000 nm depth of coatings due to a high time consumption of measurements. The depth profile data were analyzed in order to quantify the changes of silver concentration in near-surface area of films, which were then directly compared to the data from the plan view microscopy analyses.

3. RESULTS

The Ag concentration in the as-deposited Cr-N/Ag nanocomposite coating was 4.7 at.%, as measured by AES. These values of atomic concentrations correspond to weight concentrations of 11 %. The Ag was uniformly distributed along the coating thickness within an understoichiometric Cr₂N_x matrix, where x correspond to 0.62.

Fig. 1 shows plan-view SEM micrographs of the Cr₂N_{0.62}-11Ag nanocomposite film in as-deposited state and subsequently annealed for 0.5, 4 and 24 h at temperatures of 300, 400 and 500 °C, respectively. The films are composed of the matrix formed by semi-equiaxed grains with a diameter of rather less than 1 μm and individual silver agglomerates (appearing in bright contrast due to their higher backscattered electron yield versus Cr₂N). The microstructure of the Cr₂N-matrix remained almost unaffected by the annealing. On the other hand, it is clearly visible that population density of silver particles on the surface was changed by both annealing temperature and time, as documented **Fig. 2**.

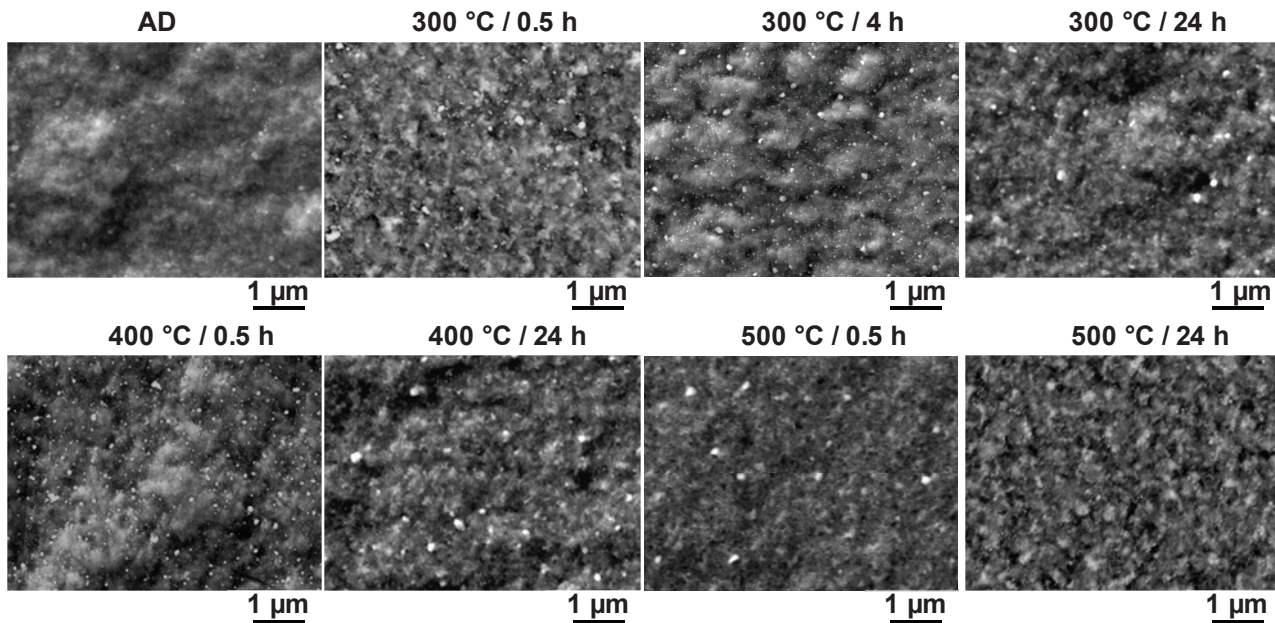


Fig. 1 SEM micrographs showing the surface microstructure of the $\text{Cr}_2\text{N}_{0.62}\text{-11Ag}$ films in as-deposited state (AD) and after annealing

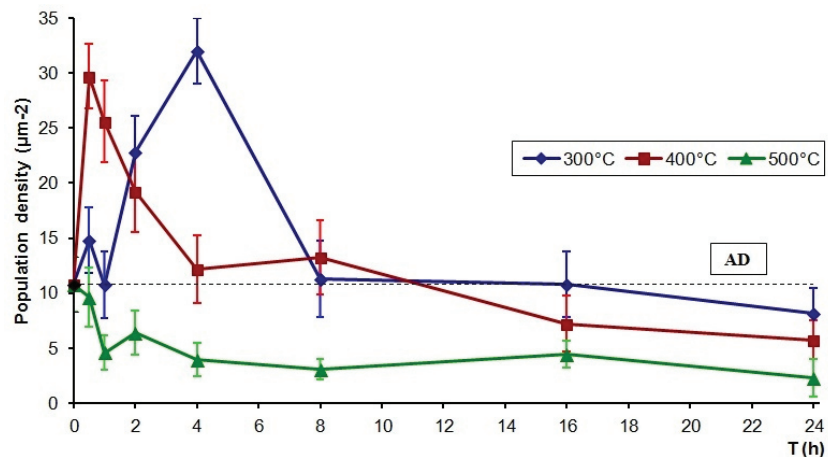


Fig. 2 Population density of silver agglomerates on surface of $\text{Cr}_2\text{N}_{0.62}\text{-11Ag}$ film as a function of annealing temperature and time

The population density of Ag-agglomerates on the coatings surface after deposition was $10.8 \mu\text{m}^{-2}$, **Fig. 2**. After annealing at temperatures of 300 and 400 °C, at first the population density increased. The maximum population densities of Ag-particles were found after annealing at a temperature of 300 °C for a duration of 4 h ($32.0 \mu\text{m}^{-2}$) and after annealing at a temperature of 400 °C for 0.5 h ($25.6 \mu\text{m}^{-2}$), respectively. Longer annealing time tends to decrease in population density of Ag-particles on the surface. After annealing at temperature of 500 °C, the population density decreased immediately and subsequently no significant changes through all annealing times were observed. The minimum values of 8.2, 5.8 and $2.3 \mu\text{m}^{-2}$ for annealing temperatures of 300, 400 and 500 °C, respectively, were found for samples annealed for 24 h.

Fig. 3a shows the concentration depth profile of silver as a functional of annealing temperature (note that “AD” denotes as-deposited state of the film) for the annealing time of 0.5 h. As evident, there is sharp local maximum of silver concentration visible near the surface irrespectively to the annealing temperature. The concentration

maximum increases with increasing the annealing temperature. In the specimen annealed at a temperature of 500 °C, there is thin near surface region where the silver content was reduced to a very low value. This is followed by rapid increase in silver amount. The explanation can be made with an assistance of the diagram in **Fig. 3b** where it is shown the oxygen content as a function of annealing temperature and depth below the surface. It is evident here that as the maximal oxygen content so the thickness of oxygen diffusion (or thickness of expected oxide layer) increases with increasing the annealing temperature.

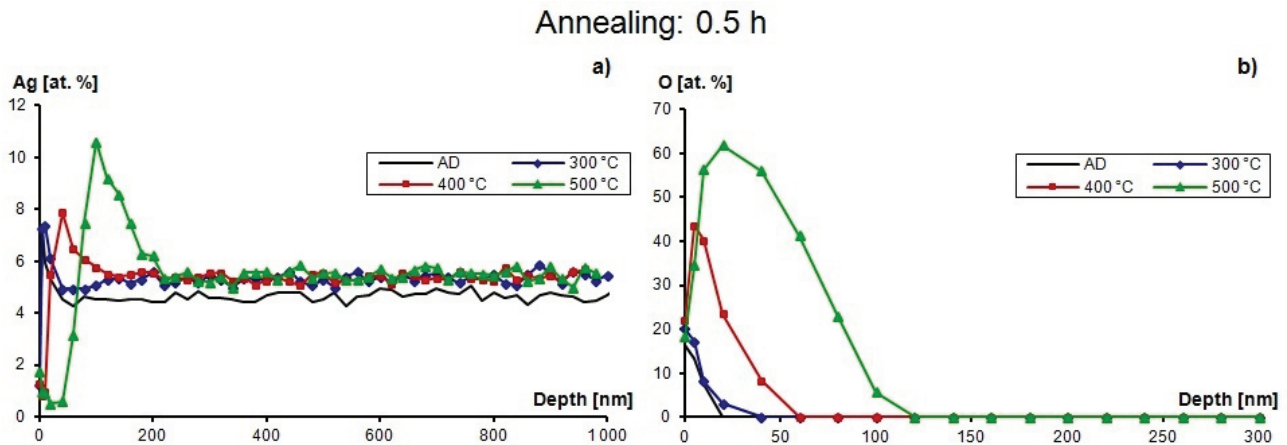


Fig. 3 AES concentration depth profiles of silver (a) and oxygen (b) for $\text{Cr}_2\text{N}_{0.62}\text{-11Ag}$ film tested in as-deposited state (AD) and after annealing at 300, 400 and 500 °C for 0.5 h

Fig. 4 shows concentration depth profiles of silver and oxygen, measured throughout the $\text{Cr}_2\text{N}_{0.61}\text{-11Ag}$ films in as-deposited state and after annealing at 300, 400 and 500 °C, respectively, for 4 h. In comparison with the results obtained after annealing of 0.5 h, there is more clearly a decrease of silver amount in near surface area for all the annealing temperatures visible, **Fig. 4a**. On the other hand, the penetration depth of oxygen (and expectedly the thickness of oxide layer) increased with increasing the annealing time, which is more remarkable for temperatures of 400 and 500 °C, **Fig. 4b**.

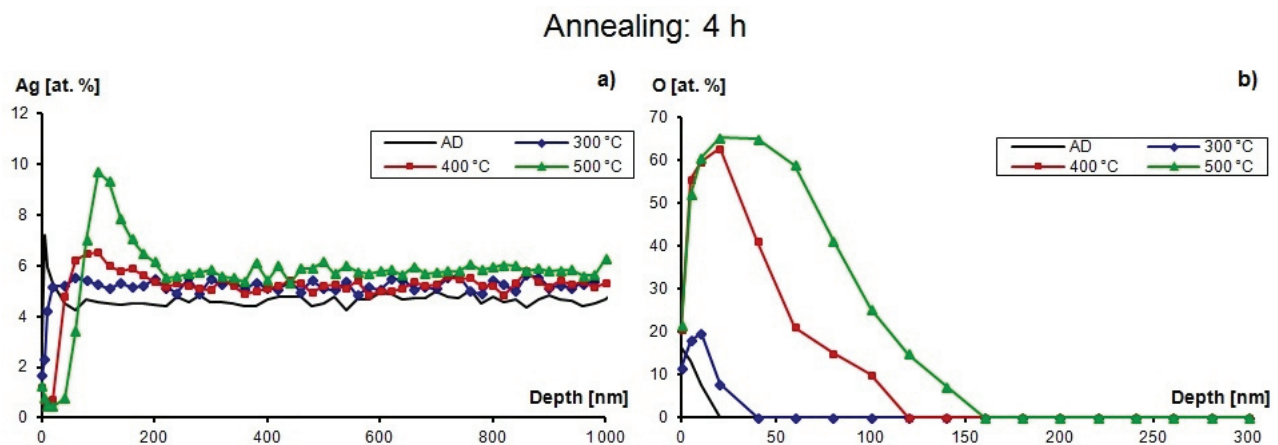


Fig. 4 AES concentration depth profiles of silver (a) and oxygen (b) for $\text{Cr}_2\text{N}_{0.61}\text{-11Ag}$ film tested in as-deposited state (AD) and after annealing at 300, 400 and 500 °C for 4 h

Post-deposition annealing for 24 h (**Fig. 5**) induces rapid depletion of the surface region by silver. The depleted areas by silver are followed by intermediate zones, which are enriched with silver in contrast. The penetration depth of oxygen further increased with increasing annealing time, **Fig. 5b**. In other words it is clearly shown

that as the maximal oxygen content so the depth of oxygen diffusion increases with increasing the annealing time and temperature, respectively.

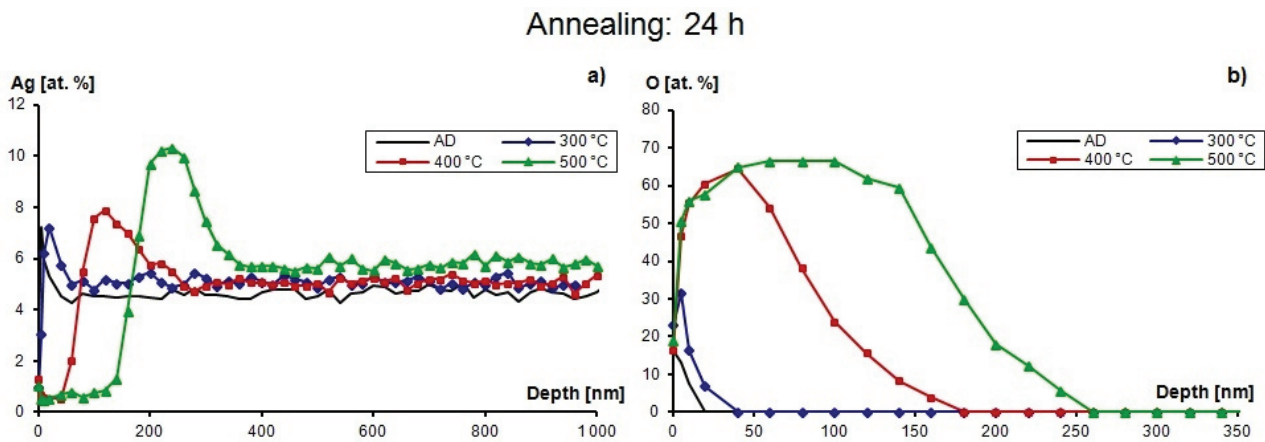


Fig. 5 AES concentration depth profiles of silver (a) and oxygen (b) for $\text{Cr}_2\text{N}_{0.62}\text{-11Ag}$ film tested in as-deposited state (AD) and after annealing at 300, 400 and 500 °C for 24 h

4. DISCUSSION

The maximum silver concentration is located beneath the oxide layers whereas it is more clearly visible when higher annealing temperatures were applied for the treatment of samples. To explain it, the following consideration can be made with this respect: At elevated temperatures, silver diffuses to the free surface of the coating, due to the gradient in the chemical potential of Ag within the Cr_2N -matrix as described for instance in [13]. The higher temperature the more intensive is the flux of Ag atoms to the surface. This is why the maximum of silver amount is more pronounced at higher annealing temperatures. The oxide layer is formed of chromium oxide Cr_2O_3 (chromia) [16]. As discussed in [17], continuous chromia layer retards the migration of silver atoms. Lowered surface content of silver, or, in other words, rapidly decreased population density of silver particles on the surface can be referred to the retarding effect of oxide layer on the migration of silver atoms to the surface. The number of silver particles presented on the surface can then be reduced by two possible ways. The first one is their evaporation due to the fact that the saturated vapour pressure of silver is very low in the air atmosphere. Detached silver atoms can then be desorbed from the surface or sublimated in a way similar to that described by Asoro et al. [18]. The second possible way why the silver particles amount was considerably reduced is the ability of silver to form a double oxide with chromium (AgCrO_2), [19]. Apart from reduced number of silver particles only coarser silver grains can be found on the surfaces while the surface is free of small silver particles after 24 h of thermal exposition. The population density of Ag particles on the surface is a result of competition between two mechanisms: sublimation, which acts to decrease in population density and diffusion of Ag from the $\text{Cr}_2\text{N}_{0.62}\text{-11Ag}$ nanocomposite film to the free surface, which induce an increase in population density. As above mentioned, oxide layer acts as a barrier against migration of silver atoms. Hence, the increasing thickness of oxide layer makes a serious contribution to the competition of above mentioned two mechanisms. Specifically, growing oxide layer makes the Ag-transport more difficult and contributes to reduction of population density of Ag-particles on the surface.

5. CONCLUSIONS

$\text{Cr}_2\text{N}_{0.62}\text{-Ag}$ composite films with 11 wt.% Ag (cca. 4.7 at.%) were deposited on ledeburitic steel Vanadis 6 at 500 °C and annealed at temperatures 300, 400 and 500 °C up to 24 h in closed-air atmosphere. The investigations have brought the following findings:

During annealing at 300 °C the population density of silver agglomerates on the surface increased with maximum at time of 4 h and subsequently started to decrease. Coalescence of silver atoms and sublimation of small silver particles are responsible for lowering of population density.

At annealing temperature of 400 °C, the oxidation of coating surface influenced the rate of silver diffusion, which is accompanied by lower population density in comparison with samples annealed at 300 °C. After 24 h of annealing, the compact chromium oxide layer was found. On the surface, there were only the coarser silver agglomerates observed. They were unaffected by silver sublimation and remained embedded on the top of oxide layer.

Both the above mentioned processes, e.g. the formation of oxide layer and the sublimation of small silver particles were even faster at a temperature of 500 °C. As a result, low population density of Ag particles on the surface and higher silver concentration in the area just behind chromium oxide layer were established.

In summary, only limited silver diffusion to the free surface and insignificant depletion of the coating by silver were observed. The obtained results infer that the key factor influencing the capability of the film to be "self-lubricating" is the deposition temperature, which affects the Ag-particle size and thereby their stability.

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