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Study of Ag transport in $Cr_2N_{0.61}$-7Ag nanocomposite thin film due to thermal exposition

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ABSTRACT

$Cr_2N_{0.61}$-7Ag nanocomposite coatings were deposited on substrates made of Cr-V ledeburitic tool steel Vanadis 6 using reactive magnetron sputtering at a deposition temperature of 500 °C. Investigations of as-deposited films and annealing experiments in closed-air atmosphere at temperatures of 300, 400 and 500 °C and the durations up to 24 h, followed by quantitative scanning electron microscopy, transmission electron microscopy, Auger electron spectroscopy and X-ray diffraction revealed that the films were composed of $Cr_2N_{0.61}$ matrix and individual silver agglomerates located along columnar crystals of the matrix. The maximal size of Ag-agglomerates was 80 nm. The surface population density of silver agglomerates increased with prolonging the annealing time up to 2 h and then decreased. The increase was more pronounced at lower annealing temperatures. This behaviour was referred to the competition between three phenomena, namely the transport of detached Ag atoms to the free surface, formation of oxide layer on the surface and sublimation of silver from the surface. At lower temperatures and/or shorter annealing times, the Ag-transport to the free surface was determined to be prevalent, thus, an increase in population density of silver agglomerates was determined. On the other hand, for higher temperatures and/or longer annealing times the population density of Ag-agglomerates rather decreased due to retarding effect of thicker oxide layer and sublimation of silver.

1. Introduction

In recent years, design and formulation of hard coatings with self-lubricating properties has become one of the hottest research topics in the field of tribological coatings. In particular, the production of new coatings architectures based on nano-composite or nano-layered structures have become very popular [1]. Nanocomposite coatings based on the incorporation of metallic and/or compound phase present an unique opportunity to achieve much better performance and durability in machining and manufacturing applications as well as in various industrial branches [2–6]. In principle, these coatings can lead to the formation of self-lubricating tribofilms that reduce the friction and wear and increase the lifetime of tools [7]. Moreover, the deposition of hard/lubricant coatings on cutting tools seems to be a very interesting alternative to reduce the enormous amounts of cooling emulsion in metal cutting and to work with minimal or no lubrication in a number of applications [8].

Inclusions of noble metals have been established as promising particles acting as solid lubricating phases in carbide [9], oxide [10,11] and nitride [12,13] matrices, as they possess sufficiently low shear strength over a suitable wide temperature range as well as stable thermochemistry allowing them to be used in both vacuum and ambient air [14,15].

Transition metal nitrides (TMN) combined with noble metals to create adaptive coatings are of particular interest as they are relatively easy to co-deposit by reactive magnetron sputtering and form nanocomposite structure, due to the lack of miscibility between the matrix and the lubricant [16].

Silver is the most common element used as an addition into the TMN 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 [17–27]. On the other hand, tribological performance of Ag-containing films are deteriorated above 500 °C since silver is less effective in providing

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lubrication when loaded because of excessive softening [28] coupled with the oxidative degradation of Cr-N/Ag films which also takes part [20,29].

Silver is embedded inside the composite matrix and its transport to the free surface is driven by strong reduction in surface energy [5,6,30]. Diffusivity of silver is naturally dependent on silver concentration, temperature and also on the microstructure of the medium through which it diffuses [6,31,32].

Mulligan's group have shown for CrN-Ag nanocomposite coatings (22 at.% Ag) grown by reactive magnetron sputtering that the temperature at which lubricant transport is activated as well as the transport rate itself are a strong function of the substrate temperature during deposition, which control Ag aggregate size [20,21]. Furthermore, the lubricant transport to the surface decreases with increasing the as-deposited Ag aggregate size, which is attributed to a decreasing (size-dependent) chemical potential. These results show that the Ag flux is controlled by the as-deposited Ag aggregate size distribution. Therefore, in order to control the Ag diffusion within the coating for a given operating temperature it is crucial to control the characteristics of as-deposited Ag aggregates since both the size and the density of the Ag particles increase with increasing the Ag content in the films.

Another finding of Mulligan's group [23,27] concerns the annealing temperature, which causes diffusion of Ag atoms from the coating to the surface, to form Ag surface grains. One of the main parameters influencing the diffusion of Ag to free surface is difference between the annealing temperature T_a and the deposition temperature T_s. In the case of $T_a \leq T_s$, only negligible Ag surface segregation occurs but in the case of $T_a > T_s$, the diffusion of silver is more significant and it increases as the $\Delta T = T_a - T_s$ increases. Unfortunately, there is a significant risk of the depletion of coating at high diffusion rates of Ag. In addition, Ag transport is no diffusion limited in CrN matrix and during diffusion, smaller particles are "consumed" to supply the silver atoms to coarser Ag-agglomerates or to migrate to the free surface. Thus, only the smaller particles (<50 nm) are capable to migrate in majority of real cases [6,20,23]. It has been also established [6,9] that silver diffusion to the surface is accelerated by shortening of the distance between the embedded silver nanograins, e.g. by increasing the amount of silver. In other words, the diffusivity of silver is concentration-dependent.

The microstructure, including the characteristics of lubricant phase (grain size and shape) as well as matrix porosity strongly affects both the solid lubricant transport rate and the development of an effective solid lubricating interface [23,27]. One can, for instance expect that the boundaries of columnar grains can act as preferential diffusion paths for migration of silver atoms to the surface. In particular, certain amount of Ag may segregate there during deposition and further form Ag-filled diffusion channels. During annealing, the Ag-filled boundaries become the preferential diffusion paths for Ag transport to the surface. The transport rate of Ag atoms depends strongly on the width and on the connectivity of the paths that increases with increasing the Ag content within the coating. At lower Ag concentrations it is expected that the diffusion paths can be disconnected which can have a retarding effect on the diffusion of Ag atoms to the free surface. During the operation, Ag atoms are removed from the surface and depleted regions are continuously replenished with Ag that diffuses to the surface when exposed at medium-to-high temperature operation [20,24].

The diffusion of silver throughout the coatings brings also some drawbacks. Due to the transport of silver atoms to the surface, the coating becomes depleted of lubricious metal and cannot act as a self-lubricated composite layer for longer time. Therefore, control of such diffusion process is required to ensure the extended lubrication. Various methods have been adopted to control the lubricant transport and to improve tribological response including the use of multi-layers and diffusion barriers, mostly made of transition metal nitrides [4,23,33,34], as well as through the addition of other alloying elements [16,35], which may limit the depletion of the lubricant and thereby prolong the lifetime of coated tools.

Our recent results on the investigations of magnetron sputtered Cr_2N-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 [18,36–38]: the predominant phases in nanocomposites coatings are Cr_2N and Ag, and no changes in the phase constitution were found after annealing at 300, 400 and 500 °C for 0.5 h. On the other hand, the friction coefficient of Cr_2N-Ag films decreased rapidly with increasing the testing temperature when alumina ball has been used as a counterpart, with the minimum at the temperatures of 400 and 500 °C for coatings with 7 and 11 wt.% Ag, respectively.

In this paper, we focused on the Ag transport mechanism within a Cr_2N matrix during annealing. The objective is to discuss the influence of parameters of annealing on structural changes and silver transport in Cr_2N film containing 7 wt.% of Ag. It should be noticed that this work is a part of comprehensive study oriented to the finding an optimal amount of silver incorporated into the $C_{r2}N$ matrix, in order to achieve the best tribological performance of the films, at their sufficient mechanical properties and adhesion on the substrate made of ledeburitic tool steels.

2. Experimental

2.1. Materials and processing

The substrate material was the PM ledeburitic steel Vanadis 6 with the nominal composition of 2.1% C, 1.0% Si, 0.4% Mn, 6.8% Cr, 1.5% Mo and 5.4% V and Fe as a balance.

The samples used for the deposition were plates with dimensions of 50 mm × 10 mm × 10 mm. After the rough machining, they were heat treated (austenitized at a temperature of 1050 °C for 30 min, nitrogen gas quenched and double tempered for 2 h at a temperature of 530 °C) to a final hardness of 60 ± 0.5 HRc. Subsequently, the samples were fine ground and polished using a 1 μm diamond slurry up to a mirror finish and cleaned with acetone in ultrasonic bath for 15 min.

The Cr_2N/Ag coatings were grown in a Hauzer-Flexicoat 850 magnetron sputter deposition system in a pulse regime with a frequency of 40 kHz. Two water cooled targets, positioned opposite one to another and at an angle of 45° with respect to the substrate surface normal, were used for the deposition. The first one was an Ag target (99.98% of purity) and the second target (cathode) was a chromium target of 99.9% purity. The output power on the Cr cathode was 5.8 kW and 0.21 kW on the Ag cathode, used to provide the desire silver content (7 wt.%). The process was carried out in a low pressure atmosphere (0.15 mbar), containing nitrogen and argon in a ratio of 1:4.5.

The samples were placed between the targets on rotating holders with a rotation speed of 3 rpm. Just prior to 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 and 500 °C for the deposition. 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.

The 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 of 300, 400 and 500 °C, using annealing times of 0.5, 1, 2, 4, 8, 16 and 24 h. Samples were placed into the preheated furnace and experiments started after 10 min, which is necessary time for equalization of the temperatures between samples and furnace atmosphere. The parameters