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Tribological properties of gradient Mo–Se–Ni–C thin films obtained by pulsed laser deposition in standard and shadow mask configurations

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ABSTRACT

Solid lubricant films were obtained by pulsed laser deposition (PLD) on steel substrates in such a way as to form an underlayer of diamond-like carbon film, and then the concentration of carbon was gradually reduced in Mo–Se–Ni–C films to obtain a pure $MoSe_x$(Ni) top layer. The use of a shadow mask configuration (SMPLD) avoids the deposition of micron- and nanometre-sized metallic particles (Ni, Mo), but the SMPLD films were characterised by relatively high Se content, reduced density and low hardness. The tribological properties of the films were evaluated using a ball-on-disk sliding test in humid air after long-term storage in laboratory conditions. For the PLD films, a relatively high friction coefficient was measured during running-in (~0.08). The friction coefficient decreased to 0.06 and did not change during the deepening of the wear track. The micro- and nano-particles were embedded into the film matrix during initial running-in and did not cause any apparent acceleration of the wear that was inhibited by the formation of a thick $MoSe_2$ tribolayer on the surface of the wear track. However, an increased wear rate of the counterpart was detected. The smooth surface of SMPLD films provides a low friction at the beginning of the test; then the friction coefficient increased gradually from 0.05 to 0.2 during the film wear, and sufficiently thick low-friction tribolayer was not found. The improved ability of the PLD films to form tribolayers could be due to their structure peculiarity and the relatively low concentration gradient of carbon in these films.

1. Introduction

Transition metal dichalcogenides (TMDs) are well known for their excellent lubricating properties in sliding contact. For most tribological applications, the protection of the bulk material by thin films is a suitable method for improving the antifriction properties and wear resistance. The most convenient and increasingly popular method to prepare these films is deposition by magnetron sputtering. In this method, the deposition parameters can be empirically optimised by varying the discharge mode (radio frequency, conventional or pulsed direct current) and changing the discharge power, the chemical composition and pressure of the gas, the location of the substrate relative to the sputtered target, the bias voltage, and the substrate temperature [1–7]. Parameter optimisation allows the formation of TMD coatings with the required structure, texture, and chemical composition.

Nevertheless, there are some common drawbacks to pure TMD coatings: a very low load-bearing capacity, low adhesion to the substrate, and a detrimental effect of the air moisture on the tribological contact. One of the most successful approaches, which has been actively developed in the present work, is to deposit a composite material, associating high strength materials with self-lubricants. Voevodin et al. [8,9] and then Nossa and Cavaleiro [10] developed the concept of nanocomposite structured coatings combining hard (WC) and self-lubricant (WS_2) phases embedded into an amorphous carbon matrix. The hardness and wear resistance of such coatings were significantly improved compared to pure WS_2; however, the coatings exhibited relatively high friction coefficients in humid air. Recently, a more complex study of TMD films doped with carbon was carried out by Polcar and Cavaleiro. In [11,12] they reviewed the results of the tribological behaviour of nanocomposite coatings composed of nanoplatelets of TMD immersed in a C-rich amorphous matrix. Three TMD materials were produced with carbon content varying between 25 and 70 at.%, namely W–S–C, Mo–Se–C, and W–Se–C systems. The parameters of the magnetron deposition process were adapted in such a way that the film did not contain hard carbide nanograins. The films showed exceptionally low friction in humid air, negligible wear and, particularly high load-bearing capacity.

In [13,14], TMD + C composite films, including Mo–Se–C and W–Se–C, were grown by pulsed laser deposition (PLD). When using PLD in standard configuration, the structure of the composite films showed several notable differences from the structure of the films obtained by magnetron sputtering. The PLD of TMD + C films resulted in the formation of a dense amorphous matrix containing nanometre-sized metal-based particles. Particle sizes varied in a range from ~5 nm to ~50 nm.

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These particles consisted of metal core and TMD-based shell. Fominski et al. [15] established that the metal core is formed at the stage of laser ablation of a synthesised TMD target (W for WSe_2 target, Mo for $MoSe_2$ target), while the shell grows as a result of condensation, migration, and redistribution of atoms during the deposition of a laser-initiated atomic flow on the surface of a growing film. For PLD of Mo–Se–Ni–C films, local ordering of atoms was detected within the amorphous matrix, causing the formation of a mixture of amorphous carbon, Mo–C, and Mo–Se phases. Increasing the carbon content caused an increase in the content of sp^3 bonds in the carbon phase, and an increase in the hardness of the films. In the case of laser ablation of TMD targets containing nickel, which is the currently used intercalating element, micron-sized Ni particles were also found on the surface of the films [13].

Mo–Se–Ni–C films obtained by shadow mask PLD (SMPLD) had no micro- or nano-particles, but these films were characterised by high selenium content and reduced density. Doping with carbon caused the formation of composite films containing Mo–Se and amorphous carbon phases as in the PLD films, but the hardness of the composite SMPLD films was significantly lower than even the hardness of the pure PLD $MoSe_x$(Ni) films [13]. A mask in the form of a thin disk was installed in the path of the laser plume from the $MoSe_2$(Ni) target, which protected the substrate from the deposition of Ni and Mo particles moving away from the target by rectilinear trajectories. The laser plume ejected from the graphite target propagated freely from the target to the substrate, bypassing the mask. In the shadowed region behind the mask, the atomic flux from TMD target was deposited only after scattering by molecules of the buffer gas introduced into the chamber for deposition. Thus, the use of the mask may affect the tribological properties of the SMPLD films both by removing the micro- and nano-particles from their volume and by changing the film growth conditions (composition, energy and angular characteristics of the deposited atomic flux).

The influence of carbon on the mechanical properties of the composite TMD + C films prepared by PLD and SMPLD was established, but the tribological properties of the composite films were not studied in [13,14]. In this paper, the results of comparative studies of tribological properties of Mo–Se–Ni–C thin film coatings obtained on steel substrates by PLD and SMPLD are presented. The films had a gradient depth distribution of solid lubricant, i.e. the $MoSe_x$ compound concentration was 100% on the film surface and decreased to zero at the interface with the substrate. This provided a relatively smooth change in the mechanical properties along the film thickness and could help to improve the adhesion of the films to the substrate. After fabrication, the samples were stored for 2 years and then the tribological tests were conducted by the pin-on-disk method in humid air.

It should be noted that the PLD regimes selected for gradient film deposition were similar to the regimes used by Fominski et al. [13] to obtain homogeneous composite Mo–Se–Ni–C films with different concentrations of carbon. It is possible to use these results to characterise the specific features of gradient Mo–Se–Ni–C films and reduce to some extent the structural and chemical analyses of the films.

2. Experimental details

A schematic diagram of the experimental set-up for PLD and SMPLD of Mo–Se–Ni–C films can be found in [14]. Laser radiation penetrated into the vacuum chamber and was scanned over the target holder by an automatic device controlled by a computer program. Two targets – $MoSe_2$(Ni) and graphite – were mounted on the holder. The angle between the laser beam and the target surface was ~45°. The substrate was placed parallel to the target surface, thus perpendicular to the particle flow. A laser beam was rapidly transferred from one target to another, so that the amount of deposited material in one cycle of irradiation of the target did not exceed one monolayer. An electro-optically Q-switched Nd:yttrium–aluminium–garnet laser (wavelength 1.06 μm) was used with a pulse duration of 15 ns, a repetition rate of 25 Hz, and a pulse energy of 30 mJ. The fluence in the laser spot was ~7.5 J/cm^2.

During fabrication of the films, a pure diamond-like carbon (DLC) layer was initially deposited from the graphite target, and then the laser beam was scanned on the two targets so that the carbon concentration decreased gradually with increasing deposition time. In forming the top layer of the gradient films, only pure $MoSe_x$(Ni) was deposited. The deposition time was identical for gradient films produced by PLD and SMPLD methods, and it was equal to 40 min. All films were deposited at room temperature of the substrate.

In the case of the PLD method, laser-produced plumes from $MoSe_2$(Ni) and a graphite target expanded freely from the target to the substrate. The residual gas pressure in the chamber for deposition in the case of PLD was no greater than 10^{-4} Pa. In the case of the SMPLD method, the mask (a thin disk of diameter 0.8 cm) was established on the path of the laser plume from the $MoSe_2$(Ni) target. The distance between the target and the mask was 2 cm and between the mask and the substrate was approximately 3.5 cm. The chamber was evacuated to a residual pressure below 10^{-4} Pa, and then argon was introduced into the chamber to a pressure of 2 Pa. Gas was used to enhance the scattering of the laser plume of the $MoSe_2$(Ni) target in the shadow area behind the mask. The laser plume ejected from the graphite target propagated freely from the target to the substrate, bypassing the mask. The diameter of the shaded deposition zone in the SMPLD configuration was ~1.5 cm.

The $MoSe_2$(Ni) target was manufactured by means of cold compacting technology using $MoSe_2$(Ni) powder obtained by self-propagating high-temperature synthesis from Mo, Ni, and Se powder. In the mixture of powders, the nickel weight fraction was ~6%. The high-temperature synthesis caused the formation of powder material containing a 2H-$MoSe_2$ phase and a small amount of metallic nickel. Details of the $MoSe_2$(Ni) target fabrication procedure can be found in [13].

The gradient Mo–Se–Ni–C films with DLC underlayer were deposited on 15-mm diameter polished disks of stainless steel type ShH-15 (analogue of 100Cr6). Samples with thin film coatings were stored for more than 2 years under laboratory conditions, where the relative humidity varied in a range from 30 to 80%. The chemical composition and depth distribution of the elements in the films were studied by Rutherford backscattering spectroscopy (RBS) of helium ions using a Van de Graaff accelerator in the Lomonosov Moscow State University, Scobeltsyn Institute of Nuclear Physics. The energy of the analysing $^4He^+$ beam was 2 MeV, and the scattering angle was 170°.

The tribological properties of the films were evaluated using a conventional ball-on-disk tribometer (CSM Instruments, Switzerland) under a normal load of 1 N with a 3-mm diameter 100Cr6 ball as a counterpart material. Three tests were performed on each sample with wear track diameter varying within the range of 0.4–1.4 cm. The sliding speed was 10 cm/s. The tests were conducted in air with relative humidity of ~40%. Characterisation of the wear tracks, the wear scars on the ball, and the wear debris was carried out using a Wyko optical profilometer, laser micro-Raman spectroscopy (MRS), and optical microscopy.

The MRS studies were performed on NTEGRA Spectra (wavelength 473 nm, NT-MDT, Russia). The diameter of the laser beam was ~0.2 μm, and the laser intensity varied widely. Preliminary studies showed the sensitivity of the Mo–Se–Ni–C films and $MoSe_2$ target to laser beam exposure. The filter was selected, allowing the spectrum of the samples to be obtained without exposing them to heat. In some cases, the spectra were measured after keeping the samples under the laser beam without using a filter. In these cases, the heating of the sample surface in air caused certain structural and chemical changes in the surface layer. Analysis of these laser-induced changes revealed useful information about the features of the structure and the chemical composition of the as-deposited films, as well as the wear track surface of these films.

Atomic force microscopy (AFM) was performed on an unworn area and a worn area of the films using an AFM Solver Pro-M