

PAPER • OPEN ACCESS

Features of pulsed laser ablation of MoS₂ and MoSe₂ targets and their influence on the tribological properties of the deposited low friction films

To cite this article: A Goikhman *et al* 2020 *J. Phys.: Conf. Ser.* **1686** 012044

View the [article online](#) for updates and enhancements.



The banner features a decorative top border with diagonal stripes in blue, orange, and yellow. On the left, the ECS logo is displayed in a green circle. To its right, the text '240th ECS Meeting' is written in a large, bold, blue font, followed by 'Digital Meeting, Oct 10-14, 2021' in a smaller black font. Below this, a promotional message reads 'Register early and save up to 20% on registration costs' in bold black text, with 'Early registration deadline Sep 13' underneath. At the bottom left of the text area, 'REGISTER NOW' is written in bold orange letters. On the right side of the banner, there is a photograph of a diverse group of people in professional attire, smiling and clapping, set against a blurred background of a conference or meeting.

ECS **240th ECS Meeting**
Digital Meeting, Oct 10-14, 2021

**Register early and save
up to 20% on registration costs**

Early registration deadline Sep 13

REGISTER NOW

Features of pulsed laser ablation of MoS₂ and MoSe₂ targets and their influence on the tribological properties of the deposited low friction films

A Goikhman¹, D Fominski², M Gritskevich², R Romanov², V Fominski², N Smirnov³

¹Immanuel Kant Baltic Federal University, Kaliningrad, A. Nevskogo St 14, Russia, 236016

²National Research Nuclear University MEPHI (Moscow Engineering Physics Institute), Moscow, Kashirskoe sh., 31, Russia, 115409

³Mechanical Engineering Research Institute of the Russian Academy of Sciences, Moscow, Bardina St 4, Russia, 119334

E-mail: vyfominskij@mephi.ru

Abstract. Laser-initiated modification of the structure and morphology of the MoS₂ and MoSe₂ targets used to obtain antifriction thin-film coatings by pulsed laser deposition were studied. Significant differences were revealed in the ablation mechanism of these materials that caused important differences in the structure formation of MoS_x/Mo and MoSe_x/Mo coatings containing submicro- and nano-scaled Mo particles. Results of the study of structure, morphology and tribological properties of these coatings (coefficient of friction, wear resistance) when testing by the technique of sliding the ball over the covered disk under different air humidity and temperatures are presented. Comparative studies have revealed the superiority of the MoSe_x/Mo coatings over the MoS_x/Mo coatings during sliding friction under varying conditions of applications in frictional unites.

1. Introduction

Solid lubricant coatings based on dichalcogenides of transition metals are one of the main substitutes for lubricants in special areas in terms of specific/complicated conditions of friction [1-3]. Such conditions include vacuum and inert atmosphere, as well as friction in units where the use of liquid lubricant is not allowed. The expansion of the field of application of solid lubricants necessitates an in-depth study of the tribological properties of perspective solid lubricant coatings, including molybdenum disulfides (MoS₂) and molybdenum diselenides (MoSe₂). Currently, there is an increasing interest in the use of these materials at low temperatures, including the conditions of negative environmental impact. Improving the methods for producing such coatings with improved properties is also an important problem in high-tech industries. [4].

The tribological properties of coatings formed by pulsed laser deposition from targets prepared by pressing powders of MoS₂ and MoSe₂ are studied. To identify factors affecting the functional properties of coatings, comprehensive studies of the processes of pulsed laser ablation of these targets, as well as structural features of the formed coatings and the correlation of the structural and phase characteristics of coatings and their tribological properties under various sliding friction conditions, were carried out.



Content from this work may be used under the terms of the [Creative Commons Attribution 3.0 licence](https://creativecommons.org/licenses/by/3.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

2. Materials and methods

To obtain MoS_x and MoSe_x coatings by pulsed laser deposition (PLD), pulsed laser ablation of MoS_2 and MoSe_2 targets was performed, respectively. The laser radiation at a wavelength of 1064 nm was applied, the duration of laser pulses with an energy of ~45 mJ was 15 ns, and the laser pulse frequency was 25 Hz. Laser fluence of ~9 J/cm² was chosen to minimize droplet formation during pulsed laser ablation of the targets. Standard configuration of PLD was used to obtain the thin-film coatings. The substrate was kept at room temperature. The deposition chamber was evacuated to a pressure of 10⁻² Pa. The coating deposition substrate represented polished 95Cr18 stainless steel discs.

The surface morphologies and composition of the targets and the coatings were studied using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDS, Tescan LYRA 3) before and after tribotests. The structure of the coatings was examined by grazing incidence X-ray diffraction (XRD) using an angle of 10° and Cu K α radiation in an Ultima IV diffractometer. The structure of the targets and the coatings before and after tribotests was also studied by means of micro-Raman spectroscopy (MRS) using a 632.8 nm (He-Ne) laser. Thin films were studied using transmission electron microscopy (TEM) and selected area diffraction (SAED) in JEM-2100 microscope.

Tribo-testing of the thin-film coatings was carried out on an Anton Paar TRB3 tribometer in a regime with reciprocating motion of a steel ball (100Cr6) with a diameter of 6 mm and a load of 1 N. The average sliding speed of the ball on the substrate with the coating was 1 cm/s. The test steel disks were mounted on a holder that was cooled with liquid nitrogen. To prevent condensation of water vapor and the formation of an ice crust, the sample was blown with a stream of argon. It was possible to maintain a disk temperature of -100°C with an optimal argon flow, as well as to effectively displace air from the region surrounding the test sample. The relative humidity of the mixture of argon and air in the environment of the sample didn't exceed RH<9%. For comparison, tribo-tests were performed at 22°C in a mixture of argon with air (RH~9%), as well as in air at RH~50%. Characterization of the wear tracks on the coatings, the wear scar on the balls, the wear debris was carried out using a Wyko optical profilometer and optical microscopy. The tests were performed both before and after ultrasonic cleaning of the disk surface. Such cleaning made it possible to remove wear particles with low adhesion to the coating. After the tribo-tests, additional studies of the samples by SEM, EDS, and MRS methods were applied also.

3. Results and discussion

Figure 1 shows typical SEM images of the surface of MoS_2 and MoSe_2 targets before and after laser irradiation. It can be seen that the MoS_2 target is characterized by relatively weak erosion under irradiation. On the surface, solidified droplets of a submicron-sized melt are visible whose composition according to EDS measurements is close to stoichiometric ($x\sim 2$). After irradiation, craters are formed on the MoSe_2 target surface and the surface composition becomes sub-stoichiometric ($x<2$). The molten layer of molybdenum selenide sufficiently wetted the target surface, and Mo nanoparticles are visible in this hardened layer.

The difference in the ablation mechanisms of the MoS_2 and MoSe_2 targets was manifested in the coatings structure deposited on steel substrates by the PLD method. Spraying the molten material from the surface of the MoS_x/Mo target caused the formation of a coating with a high content of rounded micron and submicron particles (Figure 2a). The application of a structural research complex methods showed that this coating consisted of amorphous and crystalline phases. The appearance of the crystalline phase was explained by the implantation of rounded Mo particles of submicron and nanometer size. The erosion flux from the MoSe_2 target mainly contained the vapor phase and Mo nanoparticles. This was manifested in the formation of a fairly dense and smoother MoSe_x/Mo , coating, consisting of amorphous MoSe_x and crystalline rounded Mo nanoparticles.

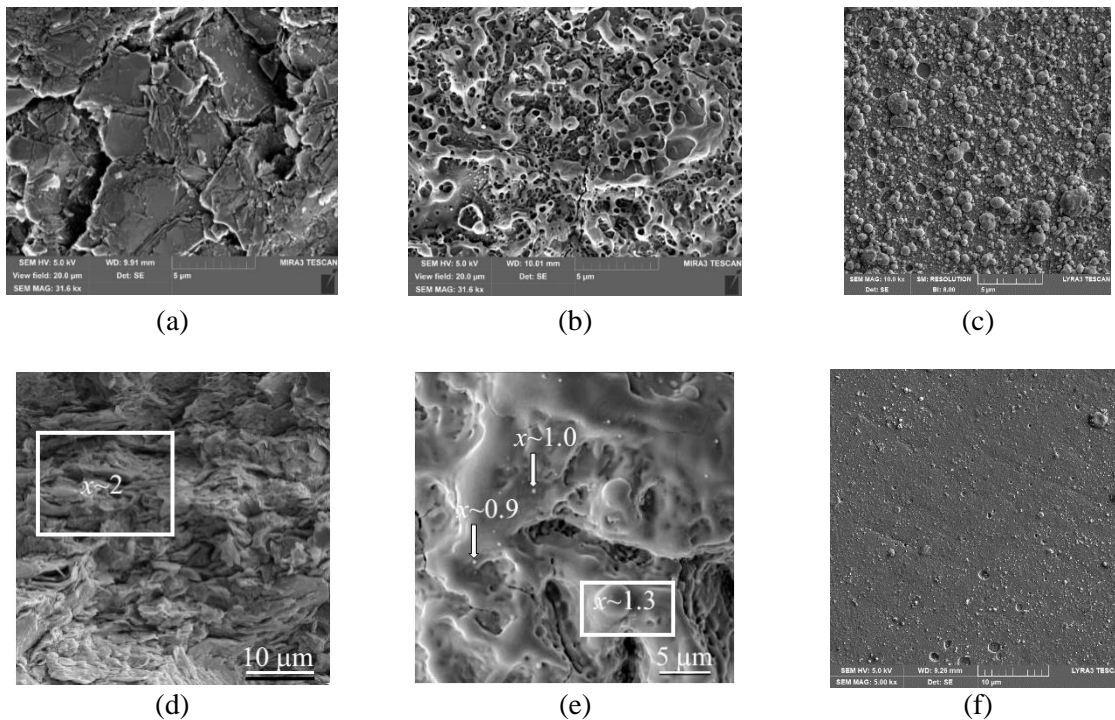


Figure 1. SEM images: (a,b) MoS₂ target; (c) MoS_x/Mo coating; (d,e) MoSe₂ target, and (f) MoSe_x/Mo (c,d) coating. The measured by EDS values of $x=\text{Se}/\text{Mo}$ are indicated.

Figure 2 shows the results of measuring the coefficient of friction for MoS_x/Mo and MoSe_x/Mo coatings under conditions that differ in humidity and air temperature. It can be seen that the antifriction properties of MoS_x/Mo coatings are largely depend on air humidity and the test temperature. In a gas environment with low humidity (RH~9%) the friction coefficient did not rise above 0.04. However, an increase in humidity to RH~50% caused an increase in the friction coefficient to 0.13. When the temperature was lowered to -100°C, the antifriction properties deteriorated significantly and the friction coefficient reached 0.4. The MoSe_x/Mo coating in a dry gas environment didn't provide as low friction coefficient (~0.06) as the MoS_x/Mo coating; however, when the test conditions were complicated, the friction coefficient increased only to 0.095.

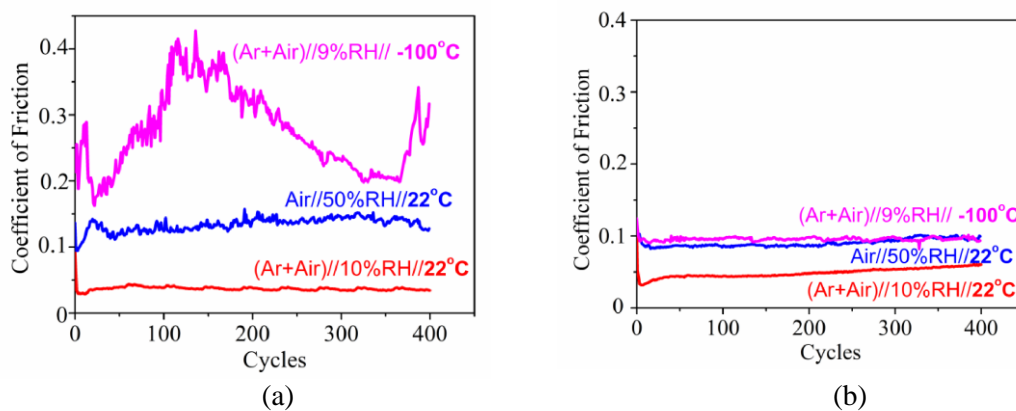


Figure 2. Characteristic evolution of the friction coefficient as a function of the cycle number for (a) MoS_x/Mo and (b) MoSe_x/Mo coatings. Ball-on-disk tribometer testing was conducted at 22 and -100 °C in an argon–air mixture (RH~9%) and in wet air (RH~50%).

To identify factors that determine the difference in the antifriction properties of MoS_x/Mo and MoSe_x/Mo coatings at low temperature, the tracks, which were formed on the samples after tribological testing, were studied (Figure 3). The sliding of the counter body over the MoS_x/Mo coating caused smoothing of the surface roughness of the coatings, partial removal of the coating material from the track (formation of a hole with a depth of ~ 200 nm) and the sticking of wear particles at the edges of the track. On the MoSe_x/Mo coating, the depth of the wear hole was only 100 nm and noticeable adherence of wear particles was not detected.

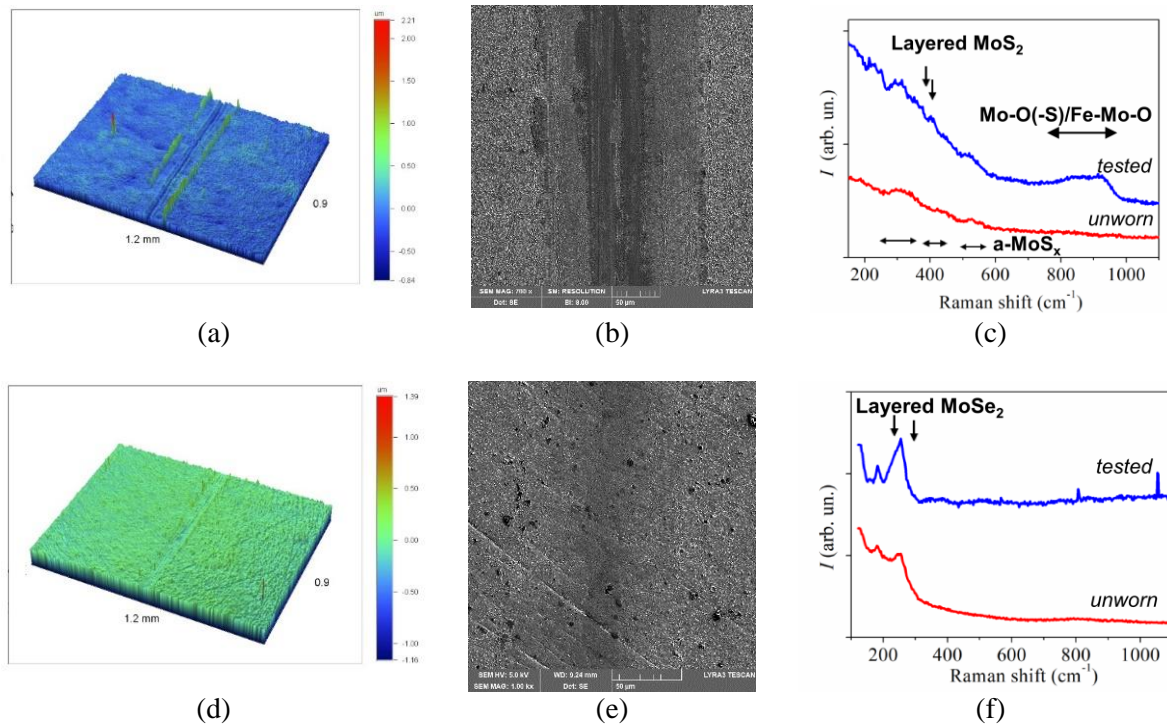


Figure 3. (a,d) 3D images, (b,e) SEM images, and (c,f) Raman spectra for (a,b,c) MoS_x/Mo and (d,e,f) MoSe_x/Mo coatings. Raman spectra were measured for unworn surface of the coatings and for the central parts of were tracks.

The MRS studies showed that the amorphous MoS_x matrix underwent weakly during the counter body sliding. After testing, weak intensity peak corresponding to the layered MoS_2 phase appeared in the Raman spectrum. There are the A_{1g} and E_{2g}^1 peaks at frequencies of 402 and 376 cm^{-1} . However, a more pronounced effect of the test was the appearance of a band from 750 to 970 cm^{-1} , which corresponded to molybdenum and iron oxides. The latter could be formed due to the adherence of wear debris of the steel counter body. The Raman spectra for the MoSe_x/Mo coating were distinguished by a more pronounced tribo-induced crystallization of the amorphous matrix and an almost complete absence of a signal from the oxide phase. For the A_{1g} and E_{2g}^1 vibrations, the frequencies of 240 and 286 cm^{-1} are typical for the layered and fairly perfect crystal structure of MoSe_2 . In the MoSe_x/Mo coating MRS spectrum, before and after the test, a peak at 253 cm^{-1} was distinguished by intensity. A peak corresponding to amorphous selenium can also lie at this frequency. It cannot be ruled out that the broadened peak in the MRS spectrum for MoSe_x/Mo coating is a result of superposition of peaks from molybdenum selenides and selenium.

4. Conclusion

Pulse laser ablation of the MoS_2 and MoSe_2 targets caused melting of the surface layer, and the molten material was distributed unevenly over the target surface. This was especially pronounced for the MoS_2

target. Spraying the melt from the MoS₂ target resulted in the formation of films with a high content of rounded particles (including Mo particles) of submicron and nanometer sizes. The structure of MoSe_x/Mo coatings turned out to be denser, and Mo particles had mainly nanometer sizes.

The MoS_x/Mo coating, despite the relatively porous structure, provided high quality antifriction properties during friction in low humidity conditions (friction coefficient ~0.04). However, its properties were greatly deteriorated during testing under complicated conditions of high humidity and low temperature, when the oxidation processes proceeded. The tribological properties of the MoSe_x/Mo coating depended on the test conditions to a much lesser extent. Under conditions of high humidity and low temperature, the friction coefficient did not exceed 0.1, which could be due to the increased oxidation resistance of Se-containing compounds in the tribofilm.

Acknowledgments

The reported study was funded by RSF (the research project 19-19-00081).

References

- [1] Guo J, Peng R, Du H et al. 2020 *Nanomaterials* **10** 200
- [2] Grigoriev S N, Fominski V Yu, Romanov R I et al. 2014 *Thin Solid Films* **556** 35-43
- [3] Fominskii V Yu, Grigoriev S N, Gnedovets A G et al. 2012 *Technic. Phys. Lett.* **38** 683–6
- [4] Fominski V Yu, Romanov R I, Fominski D V et al. 2020 *J. Friction Wear* **41(1)** 18-24