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Mechanism of tribo-induced structure modification for nanocomposite Mo–S–C–H thin film coatings

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Comparative studies of the tribological properties of solid lubricant coatings of three main types (MoS₂, *a*-C(H)) and Mo–S–C–H in an inert gas medium have been carried out. It has been established that the coefficient of friction for the Mo–S–C–H nanocomposite coating is somewhat higher than for the other two. And its wear resistance is comparable to *a*-C(H) and higher than that of MoS₂. The friction coefficient of the Mo–S–C–H coating was determined by the nature of tribo-induced surface modification. It included the formation of a nanofilm with a thickness of 6 nm and layered atomic packing characteristic of the MoS₂ phase and graphitization of the *a*-C(H) nanophase, which was accumulated in wear debris.

Keywords: nanocomposites, molybdenum disulfide, amorphous carbon, solid lubricant coatings, tribological properties.

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One of the promising directions in the field of modification of the tribological properties of contact surfaces in friction units of high-tech devices includes the creation of coatings that having small thickness can provide a stable and long-term reduction of the friction coefficient under conditions that preclude the use of liquid lubricants. The most common materials for such coatings are transition metal dichalcogenides (in particular, MoS_x) and diamond-like (including hydrogen-containing) carbon *a*-C(H) [1,2]. These materials have both specific advantages and disadvantages, which are often overcome by forming doped and nanocomposite materials [3,4]. The question of the synergistic effect of these phases on friction and wear during the formation of nanocomposite structures is of particular interest. Recently, special attention was paid to the search for coatings prone to exhibiting abnormally high antifriction properties. Usually we speak about the effect of super-lubrication if the friction coefficient does not exceed 0.01 [5–7]. One of the factors that can cause this effect is the formation of spherical nanoparticles or bundles in the contact zone of rubbing surfaces. In this case, the contact area in the friction pair decreases, and one can expect effective sliding/rolling of such particles during friction.

Reactionary pulsed laser deposition (RPLD) makes it possible to flexibly control the composition and structure of coatings in the Mo–S–C system, as well as to implement hydrogen incorporation [8]. Mo–S–C–H coatings can differ significantly in properties from the currently actively studied coatings in Mo–S, Mo–S–C and *a*-C(H) systems created mainly by the method of ion-plasma deposition [9,10]. Thus, Mo–S–C–H coatings obtained in [8] overpassed in tribological properties the *a*-C(H) coatings

when tested in humid air and inert gas at low temperatures. However, in the inert gas at room temperature the friction coefficient for the *a*-C(H) coating turned out to be the smallest, which is traditionally associated with hydrogen passivation of dangling bonds of carbon atoms. The purpose of this work is to study the tribological properties of Mo–S–C–H nanocomposite coating in comparison with MoS₂ and *a*-C(H) monophase coatings and to determine the features of the structural-phase changes in the surface layer of this coating when tested in inert gas atmosphere at room temperature.

Monophase coatings MoS₂ and *a*-C(H) were created by the RPLD method under conditions that provide rather good antifriction properties. To form MoS₂, the Mo target was ablated in H₂S at a pressure of 18 Pa. The temperature of the steel substrate was 250°C. This ensured the formation of a structure consisting of 2H-MoS₂ nanocrystals. *a*-C(H) film was created at room temperature of the substrate by laser ablation of a glass-carbon target in H₂S at a pressure of 5.5 Pa. Studies by the method of elastic forward scattering of ions shown that during RPLD the *a*-C(H) film captured sulfur in addition to hydrogen, therefore its composition was described by the formula C_{0.65}H_{0.14}S_{0.21}. When forming Mo–S–C–H coating, Mo was first ablated in vacuum, and then successive laser ablation of Mo and glass-carbon targets was carried out at pressure of H₂S equal to 5.5 Pa. The coating was deposited on the steel substrate at room temperature. The coating composition was described by the formula C_{0.49}Mo_{0.13}S_{0.28}H_{0.1}. X-ray photoelectron spectroscopy studies showed that this coating consisted of two nanophases: MoS_{1.8} and C_{0.73}H_{0.16}S_{0.11}. The ratio of atomic concentrations of these phases in

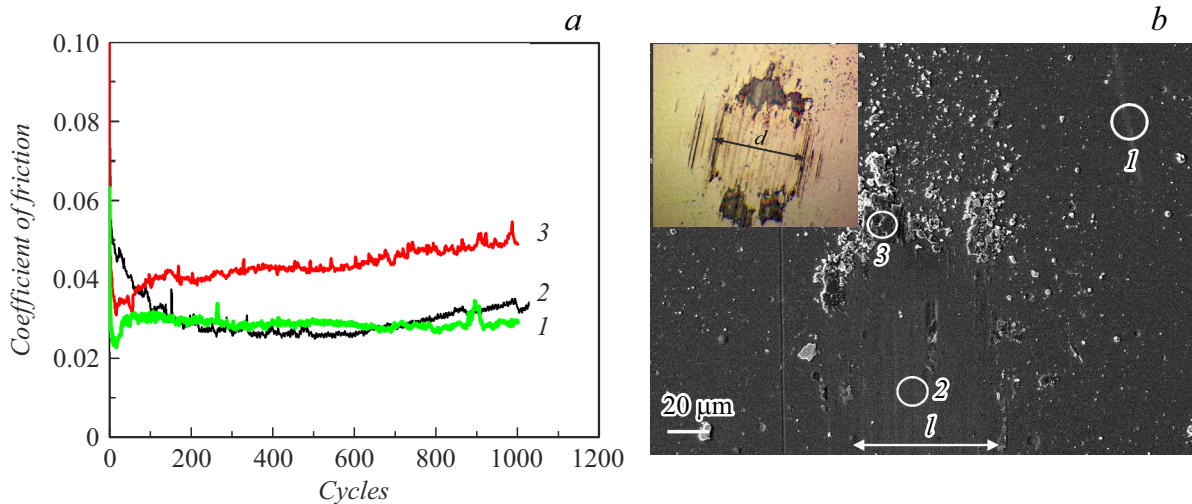


Figure 1. *a* — friction coefficient vs. number of cycles of reciprocating sliding of the counterbody over specimens coated with MoS₂ (1), a-C(H) (2) and Mo-S-C-H (3). *b* — microimages of the wear track on Mo-S-C-H coating and the counterbody (on the insert) after testing. The regions, where the Raman spectra were measured, are shown.

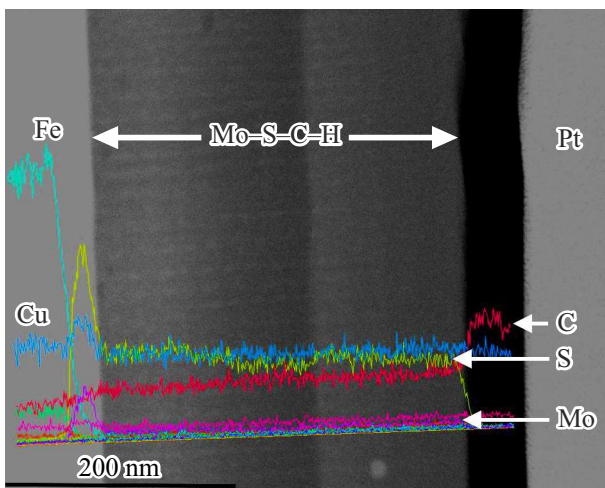


Figure 2. Elements distribution through the depth of Mo-S-C-H coating after testing.

the bulk of the coating was 2:3. Note that the sulfur introduction into the diamond-like phase contributes to the structure transformation during friction, and the formation of fullerene-like nanoparticles, which cause the effect of super-lubrication [5]. The thickness of all studied coatings was ~ 300 nm.

The study of tribological properties was carried out according to the method of ball sliding over a disk (reciprocating movements) in a medium that was created by displacing air from the test chamber with an inert gas — argon. The load on the steel ball 6 mm in diameter was 1 N. Fig. 1, *a* shows that all coatings showed good lubricating properties (friction coefficient from 0.025 to 0.045), however, the Mo-S-C-H coating was inferior in this parameter to the other two. To estimate the wear, we

used such characteristics as the width of the wear hole (l) and the diameter (d) of the contact area on the counterbody (Fig. 1, *b*). For the Mo-S-C-H coating the values for l and d were 67 and 90 μm , respectively. For MoS₂ coatings these characteristics increased to 100 and 170 μm , while for a-C(H) they did not exceed 67 and 60 μm respectively. It can be seen that the wear of Mo-S-C-H and a-C(H) coatings proceeded with the same intensity, less than for the wear of the single-phase coating MoS₂. In this case, the least wear of the counterbody was found when testing the coating a-C(H).

Fig. 2 shows the elements distribution through the depth of sample coated with Mo-S-C-H measured by energy-dispersive X-ray spectroscopy on a thinned lamella from the wear area. The distribution through depth is superimposed on the electronic image measured in cross-section mode in a dark field at a high angle. One can see uniform distribution of the elements Mo, S, C in the coating, which was preserved during wear. Studies by high-resolution transmission electron microscopy (HR TEM) showed that a layered structure was formed on the surface of the coating in local areas of protrusions. The thickness of the film with layered packing of atomic planes (marked by an ellipse in Fig. 3, *a*) reached 6 nm. The ordering of the atoms packing in layers caused the appearance of point reflections in the diffraction pattern (upper insert in Fig. 3, *a*). The distance between the atomic planes was ~ 0.6 nm according to the results of studies both by the HR TEM method and by the electron diffraction method. The basal planes in the MoS₂ compound are removed to such distance. The most probable reason for such pattern appearance is the formation of a turbostratic structure in which the basal planes of the MoS₂ lattice are parallel to each other, but rotated at arbitrary angle relative to the normal to them. HR TEM studies of the bulk of the Mo-S-C-H coating

indicated the formation of „needle“ nanoparticles (shown in the lower insert) randomly distributed in the bulk of the amorphous matrix. The nanofilm with the layered structure

and needle nanoinclusions were not detected in the study of the coating prior to testing (Fig. 3, *b*). The diffraction pattern corresponded to the amorphous structure of the coating (insert in Fig. 3, *b*).

The Raman spectra of the coating before and after testing (in the center of the track) contained peaks corresponding to the disordered a -MoS_x phase and amorphous carbon (Fig. 3, *c*). This indicated that the triboinduced formation of the film with atomic packing characteristic for MoS₂ proceeded in a thin surface layer of the Mo–S–C–H coating. It should be assumed that in the case of turbostratic packing of basal planes, the conditions for resonant light scattering, which are realized in the case of perfect packing of atoms in the $2H$ -MoS₂ lattice, may be violated.

HR TEM studies of Mo–S–C–H coatings did not reveal new carbon nanophases that could determine friction in the contact area (Fig. 3, *a*). Possibly, this is due to the fact that when creating lamellae a thin carbon film was deposited on the surface of the samples, the film „mixed“ with the carbon of the coating. However, taking into account the data of the tracks study by scanning electron microscopy, the formation of specific nanoparticles on the surface seems unlikely. Raman studies of coating wear particles showed that carbon was trapped in graphite-like particles (Fig. 3, *c*). These particles corresponded to two relatively sharp peaks at frequencies 1587 and 1355 cm⁻¹. The spectrum of wear particles also contained peaks from $2H$ -MoS₂ and FeMoS₄. MoS₂ presence was explained by the MoS₂ phase accumulation in the wear particles, the phase is removed from the surface during the counterbody sliding. The FeMoS₄ compound was formed as a result of wear of the steel counterbody during its sliding over the MoS₂ nanofilm.

Thus, when Mo–S–C–H nanocomposite coating is worn in inert gas medium, the nanophase is formed on its surface, having a layered packing of atoms, which is characteristic for MoS₂. The triboinduced synthesis of such a nanofilm from the Mo–S–C–H compound proceeds at a higher friction force than in coating containing only a sufficiently perfect $2H$ -MoS₂ phase. No signs of the formation of specific (for example, fullerene-like) carbon nanophases were found. Carbon was released from the coating and graphitized, which, together with the MoS₂ nanofilm formation on the surface, provided good antifriction properties (friction coefficient less than 0.045), however, no superlubrication effect was found at the selected load on the counterbody.

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Conflict of interest

The authors declare that they have no conflict of interest.

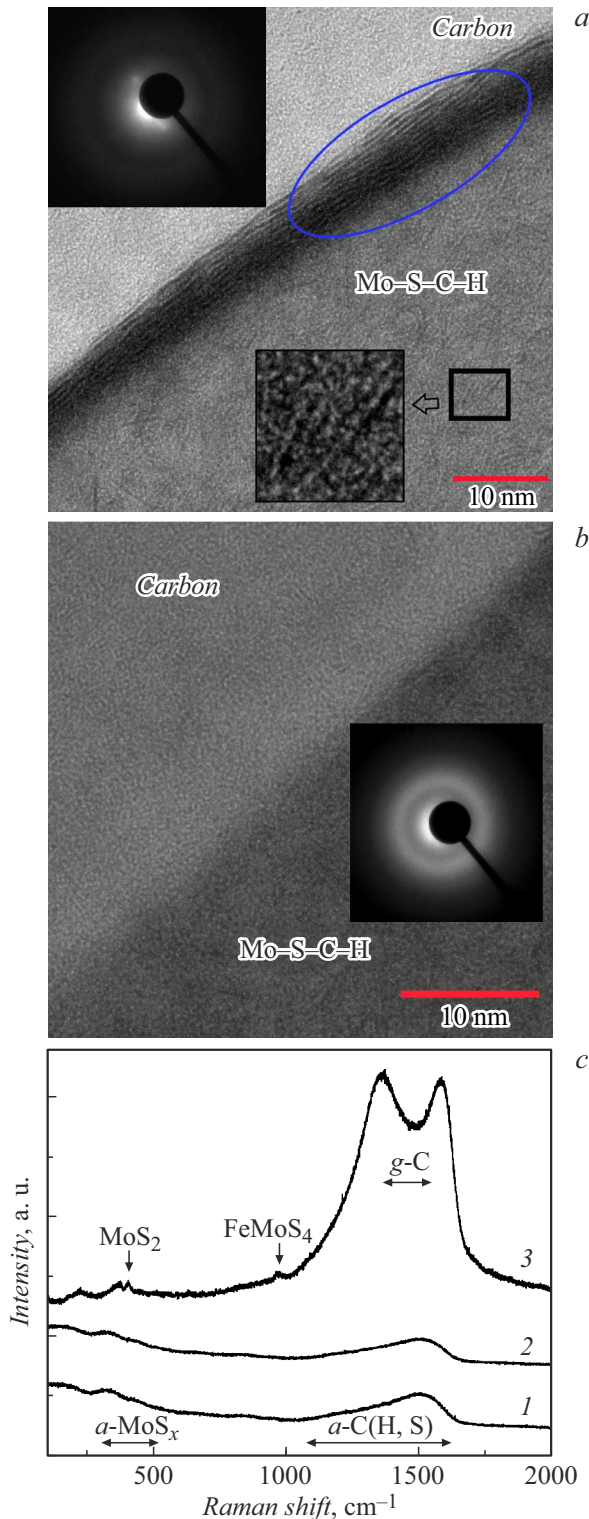


Figure 3. HR TEM image of the cross section and electron diffraction pattern (insert) of the near-surface layer of Mo–S–C–H coating (*a* — after testing, *b* — before testing). *c* — Raman spectra for the regions shown in Fig. 1, *b*.

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