Study of tribological behavior of Cu–MoS$_2$ and Ag–MoS$_2$ nanocomposite lubricants

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**Abstract**

Tribological behavior of Cu–MoS$_2$ and Ag–MoS$_2$ nanocomposite lubricant was studied. Cu nanoparticles produced by electrical explosion of copper wires and Ag nanoparticles prepared by electrospark erosion were employed as metal cladding modifiers of MoS$_2$ nanolamellar particles. The tribological tests showed Cu–MoS$_2$ and Ag–MoS$_2$ nanocomposite lubricants changed the friction coefficient of the initial grease and essentially improved its wear resistance.

**Keywords:** Molybdenum disulfide, Cu and Ag nanoparticles, Friction coefficient

**Background**

Molybdenum and tungsten disulfides due to their anisotropic layered crystal structure are characterized by unique properties. These materials are good solid lubricants and antifriction additives to oil and greases (An and Irtegov 2014), moreover MoS$_2$ is a promising material for lithium ion batteries (Wang et al. 2010). With respect to application of molybdenum and tungsten disulfides as lubricants, the synthesis and the appropriate state of dispersed materials or films play an important role. For improving tribological properties of MoS$_2$ several methods are used: decreasing the particle size (Hu et al. 2010), creation of adaptive lubricants (Prasad et al. 2000), a composite mixture with other lubricants etc. As concerns composite lubricants, Sb$_2$O$_3$–MoS$_2$ (Zabinski et al. 1993), Ag–MoS$_2$ (Zhang et al. 2012), Ti–MoS$_2$ (Renevier et al. 2001; Ilie and Tita 2007), Ni–WS$_2$ (Wang et al. 2008) composites have shown a positive effect on tribological properties in comparison with pure compounds. Copper and copper alloys are well known lubricant materials due to the zero-wear friction effect discovering in 1956 (Garkunov 2000) and widely used in composite lubricants with molybdenum disulfide, especially for applications in vacuum (Kolesnichenko et al. 1986; Merstallinger et al. 2007; Kato et al. 2003). However, a synergetic effect of excellent antiwear properties of copper and antifriction behavior of MoS$_2$ is observed in air at room temperature (An et al. 2014). The present paper is devoted to the study of the composition dependence on tribological properties of greases doped with Cu–MoS$_2$ and Ag–MoS$_2$ nanocomposites.

**Results and discussion**

An SEM image of nanolamellar MoS$_2$ (n-MoS$_2$) produced by self-propagating high-temperature synthesis (SHS) from electroexplosive molybdenum nanopowders and pure elementary sulfur is presented in Fig. 1. The particles possess a layered hexagonal shape. According to the XRD data, the main phase in the final SHS products is 2H-MoS$_2$. The prepared n-MoS$_2$ particles mixed with n-Cu and n-Ag particles in different ratios were then added to the Litol and VNIINP greases. All samples were subjected to tribological tests.

Figure 2 shows the evolution of the friction coefficient versus time for the commercial grease VNIINP undoped and doped with composites of nanolamellar MoS$_2$ and copper nanoparticles, 5 and 7 wt%, respectively. The doped grease reveals a lower average friction coefficient ($\mu_{\text{avg}} = 0.09$) than that of undoped grease ($\mu_{\text{avg}} = 0.11$). At the same time, doping the grease with the composition of nanolamellar MoS$_2$ with n-Cu leads to a friction coefficient more stable in time. Apparently, this fact is related to the metal cladding effect caused by the presence of copper nanoparticles.
Figure 3 displays the friction coefficient versus time for the n-MoS$_2$ doped with n-Cu in different ratios: 2, 7, 25, and 50 wt% n-Cu. Surprisingly, the lowest average friction coefficient ($\mu_{\text{aver.}} < 0.025$) was found for n-MoS$_2$ doped with 7 wt% n-Cu. It is lower than that of n-MoS$_2$ doped with 2 wt% n-Cu ($\mu_{\text{aver.}} \sim 0.027$). It should be noted again that copper nanoparticles impact positively on the stability of the friction coefficient in time in comparison with undoped n-MoS$_2$. The n-Cu particles clad wear fissures on the surface that leads to the formation of a soft tribofilm which allows n-MoS$_2$ particles to slide on the copper tribofilm easier than on the steel disk surface. The formation of the tribofilm was verified by the AFM measurements.

The doped Litol grease showed remarkable results for the tribological tests (Fig. 4). The lowest friction coefficient ($\mu_{\text{aver.}} \sim 0.09$) was detected for the grease Litol doped with 5% of the n-additive (n-MoS$_2$ + 7% n-Cu). This value is lower in comparison with the undoped Litol grease or doped with 5% of n-MoS$_2$.

Figure 5 and Table 1 illustrate appropriate antiwear properties of n-Cu and n-Ag additives to the Litol and VNIINP greases. 5%-additives of n-MoS$_2$ shows even an increase in wear which is apparently related to humidity conditions and a not-stable state of n-MoS$_2$ in the grease. The presence of spikes in the wear tracks is probably related to random contacts between the disk and the ball. Nevertheless, n-MoS$_2$ doped with n-Cu or n-Ag can reduce wear. In case of the VNIINP grease, wear can be even negative because of the overcladding effect when copper nanoparticles "splice" the steel surface. The AFM measurements are also in good agreement with such an assumption.
**Fig. 5** Wear tracks of the steel disk after the friction tests with (a) Litol + 5 % MoS₂, (b) Litol, (c) Litol + 5 % (MoS₂ + 7 % Ag) (d) Litol + 5 % (MoS₂ + 7 % Cu).

| Sample                          | Wear (μm$^3$ 10$^{-6}$) | Roughness of the track (nm) |
|---------------------------------|--------------------------|-----------------------------|
| Litol grease                    | 39.3128                  | 35                          |
| Litol grease +5 % n-MoS₂        | 172.53358                | 210                         |
| Litol grease + 5% (n-MoS₂ + 7% n-Cu) | 127.3898                | 32                          |
| Litol grease 5% (n-MoS₂ + 7% n-Ag) | 32.69368                | 93                          |
| VNIINP grease                   | 15.15992                 | 25                          |
| VNIINP grease + 5 % (n-MoS₂ + 7% n-Cu) | -2.17288                | 102                         |
Conclusions

Composite greases containing nanolamellar MoS2 doped with Cu and Ag nanoparticles were successfully prepared for tribological tests. The performed tribological tests showed the better anti-friction performance for both the solid n-MoS2 lubricant doped with copper nanoparticles and the Litol and VNIINP greases doped with n-MoS2 with copper nanoparticles. Electroexplosive copper and electroerosive silver nanoparticles can improve the n-MoS2 tribological performance due to a visible rise in antwear characteristics. At the same time, we can expect essential improvement of oxidation stability of the greases doped with the studied metal nanoparticles, especially with n-Ag. Another explanation for the improvement of the properties is related to a synergistic effect in using nanolamellar molybdenum disulfide and metal cladding additives of Cu and Ag nanoparticles.

Experimental

MoS2 nanolamellar particles (n-MoS2) produced by self-propagating high-temperature synthesis (SHS), as well as copper (n-Cu) and silver nanoparticles (n-Ag) obtained by electrical explosion of wires (EEW) and electrospark erosion, respectively, were used for preparing a composite lubricant. SHS of metal sulfides from metal nanopowders is discussed in Irtegov et al. (2012). Conditions and parameters of electrical explosion of copper wires are presented in An et al. (2014). The initial powders were analyzed using an X-ray diffractometer Shimadzu XRD-7000 diffractometer (CuKα irradiation) and a scanning electron microscope (JSM-7500FA, JEOL). In order to minimize agglomeration, the nanoparticles were subjected to ultrasonic treatment in an organic solvent before the preparation of the greases. For tribological tests MoS2 nanolamellar particles and Cu nanopowder are mechanically mixed during 30 min. Copper content in composite lubricant was 2, 7, 25 and 50 wt%, respectively. Besides, a solid lubricant, complex soap based greases (LITOL and VNIINP) with Cu–MoS2 additives were produced by dispersing using ultrasonic bath. Before dispersing, viscosity of greases was decreasing by addition of hexane. After dispersing composite greases are dried at room temperature during 24 h. Tribological investigations of pure nanolamellar MoS2, composite Cu–MoS2 lubricants and greases were carried out by “ball-on-disk” PC-Operated High Temperature Tribometer TXT-S-AH0000, CSEM. The wear scar was explored on a noncontact profilometer Micro Measure 3D Station, STIL. All tests were carried out using a 30 mm diameter medium-carbon steel disks as the friction body, and a vanadium-cobalt ball of diameter 3 mm was used as the counterface. The tests were run using a load of 5 N and sliding speed of 5 cm/s, with track diameter 3 mm, duration of tests was 30 min. The mean contact pressure was 0.56 N/mm². After friction tests surface of wear scars were analyzed using an atomic force microscope Ntegra Aura (NT-MDT, Russia).

Authors’ contributions

VA carried out the main conception and the main tribological experiments, participated in the analysis and interpretation of data. EA and IS carried the main tribological experiments and participated in the analysis interpretation of the data obtained. VB, NB, MK participated in the development of the main conception and its interpretation. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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