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Research Article

Tribological Properties of Nanolamellar MoS_2 Doped with Copper Nanoparticles

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This study aimed at examining the tribological properties of nanolamellar molybdenum disulfide doped with copper nanoparticles. Nanolamellar molybdenum disulfide was produced using self-propagating high-temperature synthesis via the reaction between elementary sulfur and nanosized molybdenum powder prepared by electrical explosion of wires. Copper nanoparticles were also prepared by electrical explosion of copper wires. Comparative tribological tests were carried out for nanolamellar and commercial molybdenum disulfides doped with 7 wt.% of copper nanoparticles. It was demonstrated that doping copper nanoparticles additives reduce wear of the friction body when using both commercial and nanolamellar molybdenum disulfide.

1. Introduction

A large amount of research has been devoted to the study of tribological properties of lamellar transition metal dichalcogenides (TMDC) like molybdenum disulfide (MoS_2). Remarkable antifriction and antiwear properties of molybdenum disulfide in an inert atmosphere or vacuum are explained by its lamellar structure resulting in low shear strength. Martin et al. [1] speculated about superlubricity of molybdenum disulfide. Pure MoS_2 is supposed to satisfy the condition of superlubricity taking into account frictional anisotropy of the shear oriented low energy basal planes. Jamison and Cosgrove [2] correlated the lowest friction coefficient to the axial ratio c_0/na_0 which might not exceed 1.87, whereas it is equal to 1.95 for 2H-MoS_2. Molybdenum disulfide is used as a solid lubricant [3], a tribological coating [4], or an additive to lubricants [5].

Some papers are concerned with antifriction and antiwear performances of these materials in the nanostructured state. Miura et al. [6] have theoretically estimated superlubricity of molybdenum disulfide nanoflakes and supposed that the Amontons-Coulomb law should hold for it. They established that the coefficient of friction decreased down to 0.003 between two MoS_2 surfaces. It has been reported that the addition of the MoS_2 nanotubes to polyalphaolefin oils reduced the coefficient of friction by more than 2 times and the wear by as much as 5–9 times [7]. However, some papers [8] reported the friction of the MoS_2 nanoparticles to be significantly higher than that observed for the large particles. In [9], the authors have tested tribological performance of round shape inorganic fullerene-like MoS_2 nanoparticles that were synthesized by reacting MoO_3 vapor with H_2S in a reducing atmosphere. They have found such particles are able to exfoliate due to the fast formation of a tribofilm made of MoS_2 nanosheets. It has been also reported that the coefficients of friction between silicon AFM tip and MoS_2 nanotube or MoS_2 nanoonion are much below the relevant values for flat single crystal MoS_2 or graphite [10]. The weakly supported tubes revealed the coefficient of friction of 0.023 ± 0.005. The studies of the tribological properties of nanostructured molybdenum disulfide are, therefore, of great interest.

Nevertheless, some conditions, for example, high humidity and temperatures, impose limitations in its application areas. Nowadays various chemical additives are used in order to enhance operating performance of lubricants. Over the last decade, the number of studies on the effects related to doping TMDC with small additives of various metal nanoparticles has been reported [11–13]. The interest in doping dichalcogenides like molybdenum disulfide is associated

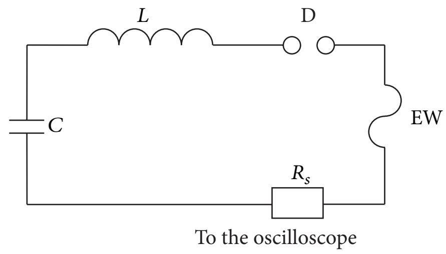


Figure 1: Principal scheme of the setup for the fabrication of nanoparticles by electrical explosion of wires: C: capacity, L: inductance, D: disconnector, R_s: shunting resistance, and EW: exploding wire in the explosion chamber.

with the idea for improving their oxidation stability with simultaneous additional antifriction or antiwear effects [14–16]. Some papers are devoted to the studies of the effect of copper particles on friction. For example, the authors of [17] considered wearless friction conditions in the bronze-steel pair lubricated by dispersed nanosized copper clusters in an aqueous glycerin mixture. Bao and coworkers [18] reported that the friction coefficient of the Cu-MoS_2 powder metallurgy material/bronze pair and wear rates of MoS_2 powder metallurgy material are greatly decreased.

This paper focuses on the study of tribological properties of nanolamellar molybdenum disulfide doped with copper nanoparticles. We have expected a synergistic effect by modifying nanolamellar MoS_2 with copper nanoparticles due to their joint tribological action in the friction area. It is supposed that chemical stability of such a system will be better. It is also expected that the copper nanoparticles will cause a metal cladding effect of rubbing surfaces and reduction of wear.

2. Experimental Procedure

2.1. Materials. Self-propagating high-temperature synthesis (SHS) was used for the fabrication of nanolamellar molybdenum disulfide. A similar synthesis method for fabrication of metal sulfides for tribological applications has been reported in [19]. Synthesis was performed via reaction of nanosized molybdenum powder with pure elementary sulphur. The nanosized molybdenum powder was produced by electrical explosion of molybdenum wires (EEW) in argon. The EEW is connected to a high current density ($j > 10^{10}$ A/m^2) [20] and a high metal heating rate (~10^{10} K/s) characterizing the process up to high temperatures ($T > 10^4$ K) [21]. The EEW method allows manufacturing a large variety of metals and compounds, including copper nanoparticles used in this study. Electrical explosion of wires is carried out in the setup the principal scheme of which is given in Figure 1.

Copper nanoparticles were produced by electrical explosion of copper wires the diameter of which was $d = 0.28$ mm. The length of the wire, fed between the electrodes in the explosion chamber using a feeding unit, was $l = 65$ mm. The electrical explosion was carried out in the argon atmosphere at a pressure of 2.5 atm; $U = 24$ kV, $C = 3.48\,\mu$F, and $L = 0.75\,\mu$H. According to the BET method analysis, the specific surface area of the copper nanopowder was 6.9 m^2/g.

In order to organize an exothermal reaction for the synthesis of nanolamellar molybdenum disulfide, cylindrical pellets of 32 mm in diameter were prepared. The pellets were compacted from a stoichiometric mixture of nanodispersed molybdenum powder and pure elementary sulphur. The process of self-propagating high-temperature synthesis of nanolamellar molybdenum disulfide was carried out using the experimental setup presented in [22]. The setup consists of a hermetic chamber which can function at a limit pressure of 50 atm. The chamber is equipped with a working gas intake and a sample holder. Combustion of the sample was initiated with a nichrome filament. A tungsten-rhenium thermocouple was used for the control of the combustion temperature. Its hot junction was located in the pellet hole. The cold ends were connected with an oscilloscope. The visual control of the combustion process was carried out through a special quartz window.

The as-synthesized products were easily disintegrated silvery-black agglomerates. They were ground and washed out from sulphur traces in hexane under ultrasonic treatment. After drying, the obtained powders were analyzed using an X-ray diffractometer Shimadzu XRD-7000 diffractometer (CuK_α irradiation), a scanning electron microscope (JSM-7500FA, JEOL).

2.2. Sample Preparation for Tribological Tests. The current tests of the friction coefficient of the undoped, nanolamellar, and commercial molybdenum disulfides were carried out by "ball-on-disk" PC-Operated High Temperature Tribometer (THT-S-AX0000, CSEM). The wear scar was explored on a noncontact profilometer (Micro Measure 3D Station, STIL, France). Medium-carbon steel disks of diameter 30 mm, height 4 mm, and surface roughness $R_a = 60$ nm were used as the body, and a hard alloy ball of diameter 3 mm was used as the counterbody. The normal load was 5 N and 10 N, the duration of test run was 30 min, the linear speed was 5 cm/s, and the wear track radius was 3 mm. All tests were carried out in lab environment.

After the tribological experiments, the used disk surface was cleaned with an organic solvent (acetone) and was explored with an optical microscope. The wear track area equal to 2 mm × 1 mm was scanned and the volume wear was calculated by six points using profilometer software. After the treatment of the obtained track images, the surface areas above and below the baseline were determined. The wear volume was then calculated using the following formula (μm^3):

$$V = (S_- - S_+) \cdot \pi D_m, \tag{1}$$

where S_+ is the sum of the area above the baseline, μm^2; S_- is the surface are below the baseline, μm^2; D_m is the diameter of the wear track, μm.

The lubricated track asperity was also determined.

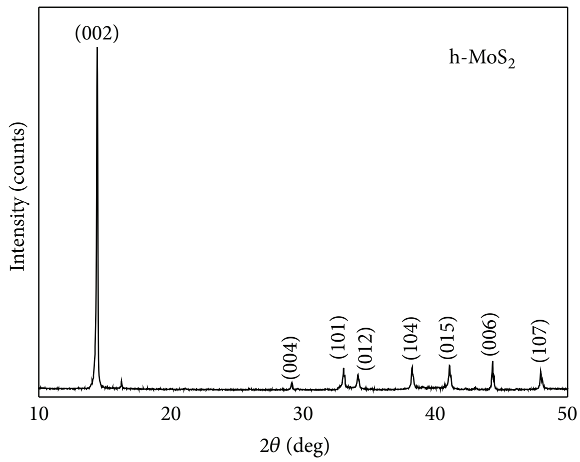


Figure 2: XRD pattern of nanolamellar MoS_2.

3. Results and Discussion

3.1. Physicochemical and Tribological Characterization. As-prepared molybdenum disulfide was subjected to X-ray diffraction analysis and scanning electron microscopy. The XRD analysis results showed that the main phase in the final products is 2H-MoS_2 (Figure 2). The dominant crystal orientation has the basal plane (002). Higher intensity of the (002) peaks evidenced the elongated shape of the crystallites. The lattice parameters for hexagonal MoS_2 are $a = 3.161$ Å and $c = 12.27$ Å. The coherent scattering domain size was determined according to Scherrer's equation and found to be in the range of 50–60 nm. This data correlates well with the scanning electron microscopy analysis. Such structure of nanolamellar molybdenum disulfide allows us to predict the formation of a stable nanoscale tribofilm during friction.

The nanolamellar or commercial molybdenum disulfides were mechanically mixed in a mortar with 7 wt.% of copper nanoparticles prepared by electrical explosion of wires and then treated in a hexane suspension in an ultrasonic bath and further natural drying. Nanosized copper presented particles of 50–80 nm with a spherical, slightly faceted shape (Figure 3(a)). Such a shape is characteristic for the copper nanoparticles produced by electrical explosion of wires. The faceted shape of electroexplosive copper nanoparticles is connected to their passivation process with a very thin film of copper oxide after electrical explosion of wires. Passivation is a standard procedure for the metal nanoparticles produced by EEW in order to reduce their pyrophoricity. When increasing the energy input into the wire and decreasing the average particle size, chain-like structures of the small particles form around the bigger ones. An essential part of these particles is sintered between each other (formation of necks), whereas the particles begin to take irregular faceted shape. Such chain-like structures of small particles group around the bigger ones. Irregular shape can be also characteristic for copper nanoparticles produced both by physical and by chemical methods. Mostly, it is related with protective oxide shell. It is supposed that additives of passivated copper nanoparticles will provide chemical stability of their composites with nanolamellar molybdenum disulfide. In spite of higher cost, electroexplosive nanosized copper reveals excellent metal cladding properties according to certain sources [23]. The same behavior can be predicted for commercial MoS_2 doped with copper nanoparticles which is shown in Figure 3(b).

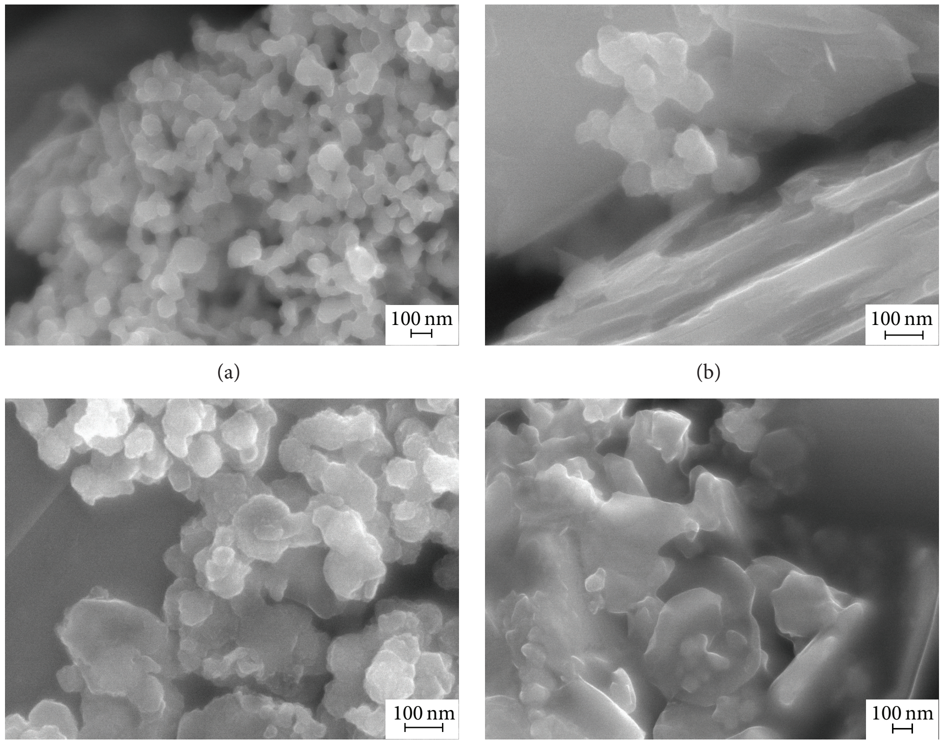
Figures 4 and 5 show the coefficients of friction and three-dimensional images of the wear tracks that obtained commercial and nanolamellar MoS_2 undoped and doped with copper nanoparticles at a friction load of 5 N, respectively. Evolution of the coefficient of friction over time is more stable for undoped nanolamellar molybdenum disulfide: the mean μ value is approximately 0.01 (Figure 4, curve 3). The lower μ value can explain that the tribological tests were performed under low humidity conditions. The coefficient of friction for the nanolamellar molybdenum disulfide doped with copper nanoparticles evolves in a less stable manner (Figure 4, curve 4) and is characterized with higher μ values. The doping copper nanoparticles can temporarily agglomerate during friction and, therefore, provoke instability of the coefficient of friction. Nevertheless, the formation of a nanoscale copper tribofilm can lead to the stability of the coefficient of friction over time.

Figures 3(c) and 3(d) show that more copper nanoparticles adhered to MoS_2 nanolamellar particles after the tribological tests. The three-dimensional images (Figure 5) illustrated that the wear scars for undoped commercial and nanolamellar MoS_2 are deeper than those for doped powders. This is a visual evidence of a so-called metal cladding effect during friction with copper nanoparticles.

When increasing the friction load up to 10 N, nanolamellar molybdenum disulfide reveals a relatively high coefficient of friction. It can be related with the fact that nanolamellar MoS_2 absorbs better water vapors from the atmosphere and can decompose at a higher friction load faster than the other samples (Figure 6). Undoped commercial MoS_2 demonstrated the coefficient of friction lower than that for nanolamellar disulfide but higher than those for the doped samples. Doped nanolamellar molybdenum disulfide showed the lowest coefficient of friction at the limit of the μ values around 0.02.

Table 1 regroups the profilometry data on the wear degree (according to formula (1)) of the disks lubricated with different MoS_2 containing compositions. As we expected, the highest wear volume is characteristic for undoped commercial MoS_2 at both friction loads. For the friction load of 10 N, the wear volume for commercial powder doped with copper nanoparticles is 1.5 times higher than that for undoped commercial MoS_2. For the load of 5 N, wear negative values were obtained for both commercial and nanolamellar molybdenum disulfides. Supposedly, it can be explained that the wear track is "overclad" with copper nanoparticles at a lower friction load. At the load of 10 N, this effect is not observed.

3.2. Possible Mechanism of the Action of Copper Nanoparticles on the Nanolamellar Disulfide Tribological Performance. Copper nanoparticles can make a metal cladding effect of sliding surfaces. At the same time, they can adhere to the particles surface of nanolamellar molybdenum disulfide.



(a) (b)

(c) (d)

Figure 3: SEM images for copper nanoparticles (a), commercial molybdenum disulfide doped with nanoparticles (b), and nanolamellar molybdenum disulfides doped with Cu nanoparticles before (c) and after the tribological test (d).

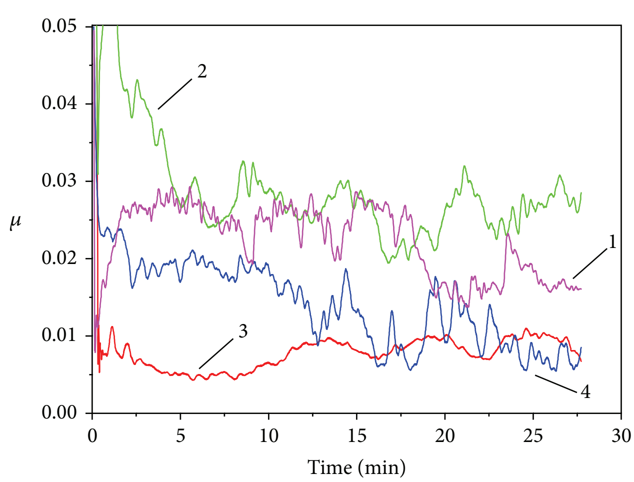


Figure 4: Coefficient of friction for commercial MoS_2 powder without (1) and with (2) copper nanoparticles and for nanolamellar MoS_2 without (3) and with (4) copper nanoparticles at a friction load of 5 N.

Table 1: Profilometer results of wear track.

Sample	Depth of wear track (μm)	Wear volume ($\mu m^3 \cdot 10^{-3}$)
MoS_2-NL* (5 N)	0.42	2.0
MoS_2-C** (5 N)	0.57	3.5
MoS_2-NL + Cu nano (5 N)	0.11	Negative value
MoS_2-C + Cu nano (5 N)	0.18	Negative value
MoS_2-C (10 N)	1.22	624.6
MoS_2-NL + Cu nano (10 N)	0.82	320.3
MoS_2-C + Cu nano (10 N)	1.12	421.11

*MoS_2-NL: nanolamellar molybdenum disulfide.
**MoS_2-C: commercial molybdenum disulfide.

Copper can reveal a very good ability for adhesion to the surface of the steel disk. Figure 7 schematically illustrates the possible mechanism of the tribological action of nanolamellar molybdenum doped with copper nanoparticles. Copper nanoparticles can penetrate to the friction area (wear track) autonomously or due to temporary adhesion nanolamellar particles of molybdenum disulfide (Figure 7(a)). However, the adhesion force to the steel disk surface is significantly stronger than the van der Waals interactions between the surfaces of MoS_2 and Cu particles. The copper nanoparticles, therefore, adhere intensively to the wear track surface. The effect of the wear track cladding on copper nanoparticles occurs (Figure 7(b)). A copper tribofilm forms when copper nanoparticles interact with the wear track surface. Permanent penetration of MoS_2 nanolamellar particles in the friction

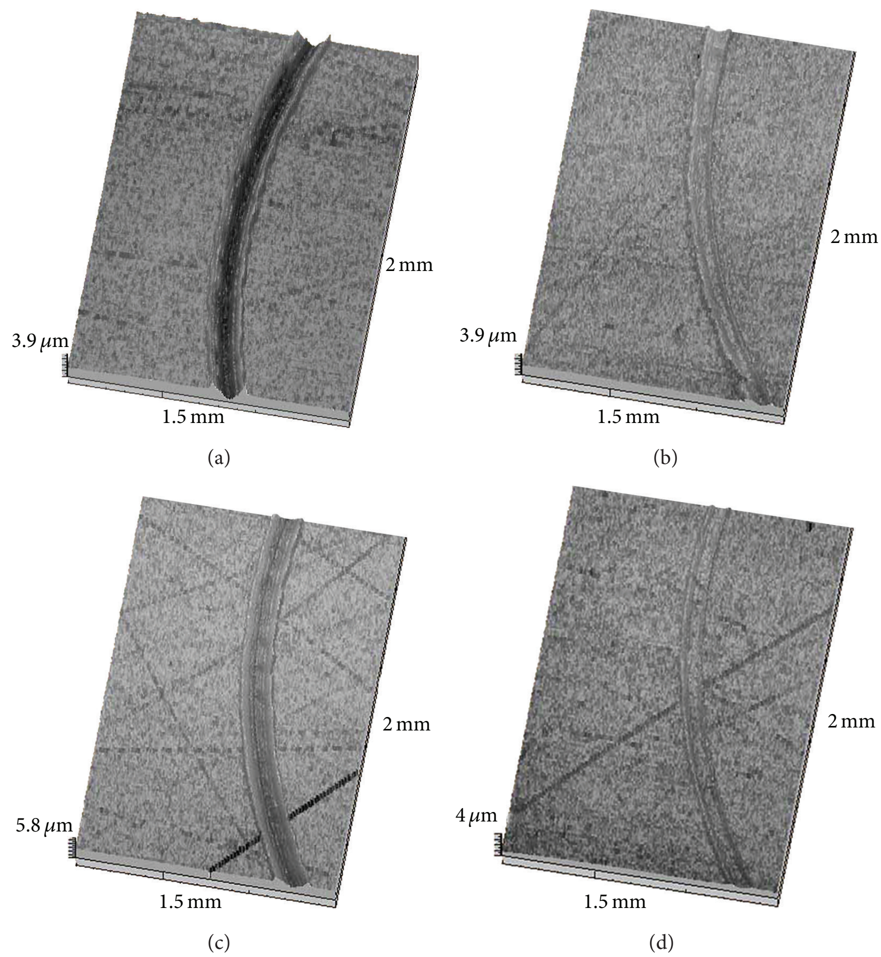


Figure 5: Three-dimensional images of the wear scars for the samples lubricated with undoped (a) and doped (b) nanolamellar MoS_2 (a) and undoped (c) and doped (d) commercial MoS_2.

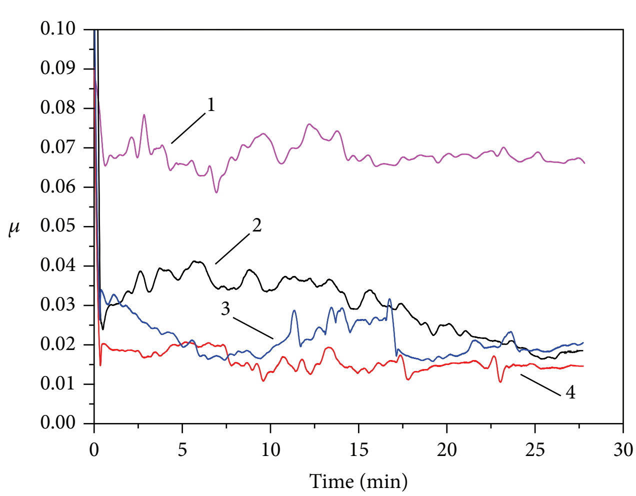


Figure 6: Coefficient of friction for undoped nanolamellar MoS_2 (1), commercial MoS_2 undoped (2) and doped with copper nanoparticles (3), and nanolamellar MoS_2 doped with copper nanoparticles (4) at a friction load of 10 N.

area ensures smooth sliding conditions for copper nanoparticles. Such a mode allows formation of a multilayered cladding copper tribofilm.

We can, therefore, observe a synergistic effect of the combined action of nanolamellar molybdenum disulfide and copper nanoparticles on the friction area. A significantly weaker similar effect is characteristic for commercial molybdenum disulfide doped with copper nanoparticles. It is necessary to take into consideration possible agglomeration of the used nanoparticles which can lead to nonuniform dispersion. This problem can be solved when using these nanoparticles in oil based lubricants with special solvents in which they can form stable suspensions.

4. Conclusions

For the first time, a comparative study of tribological properties of commercial and nanolamellar MoS_2 doped with copper nanoparticles prepared by electrical explosion of wires was performed. The experiments were carried out

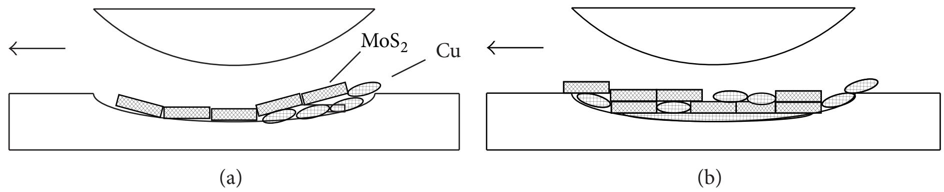


Figure 7: Schematic diagram describing the possible mechanism of the tribological action of nanolamellar disulfide doped with copper nanoparticles.

at room temperature. It was found that, at a load of 5 N, the coefficient of friction of nanolamellar MoS_2 doped with copper nanoparticles is lower than that for doped commercial MoS_2. When increasing the load up to 10 N, doped and undoped nanolamellar molybdenum disulfide have demonstrated a lower coefficient of friction in comparison with that of commercial powder. It was also explored that the introduction of the copper nanoparticle additives essentially reduces wear of the friction body surface. Most likely it is due to the metal cladding effect of the wear track with the tribofilm formed by the copper nanoparticles.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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