Tribological Properties of SiO₂@Cu And SiO₂@MoS₂ Core-Shell Microspheres As Lubricant Additives

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Abstract

Herein, core-shell structural $\text{SiO}_2@\text{Cu}$ and $\text{SiO}_2@\text{MoS}_2$ microspheres were prepared using SiO_2 as hard core, Cu and MoS_2 as shell. As lubricant additives were introduced into base oil (PAO 40), their friction-reduction and wear-resistance were investigated in detail. Comparing with onefold additive (SiO_2 , Cu and MoS_2), such core-shell structure additives can improve the tribological behaviors at the Hertz contact stress range of 1.26 ~ 2.72 GPa ($\text{SiO}_2@\text{Cu}$ reduces the friction and wear up to 32.47% and 67.86% at 2.72 GPa, respectively). Besides, the tribological properties of $\text{SiO}_2@\text{Cu}$ microspheres are superior to that of $\text{SiO}_2@\text{MoS}_2$ (the wear volume was reduced by 48.45% at 2.72 GPa). The excellent tribological behaviors of $\text{SiO}_2@\text{Cu}$ microspheres can be ascribed to its structural advantage, the synergistic effect of hard SiO_2 core and Cu shell. The rolling effect of SiO_2 , easy-shearing and self-repairing of Cu shell offer a synergistic lubrication function and form a dense protection film, thereby contributing to the optimal lubrication performance.

Introduction

Energy losses across all mechanical systems are primarily attributed to friction and wear of moving elements. Therefore, lubricants are used to improve the energy efficiency of automobile engines and industrial machinery, extend service intervals, and enhance durability and reliability [1–4]. During the past decade, an important research topic in the field of tribology is to explore high performance solid lubricant additives with low friction and high wear resistance, in view of their small size and thermal stability [5–7]. With the development of nanotechnology, a considerable number of solid particles with different structures have been fabricated to regulate the tribological behaviors of lubricating oil [2, 8]. But it cannot be ignored that onefold solid additive has some drawbacks. On the one hand, hard solid particles such as SiO_2 and ZnO will easily scratch the contact surface causing abrasive wear, and soft particles such as Cu and PMMA cannot be suitable for harsh conditions due to their poor mechanical strength. On the other hand, the traditional mechanical mixing method is easy to produce problems such as phase separation or uneven dispersion, which cannot achieve the technical requirements of low friction and wear resistance under harsh working conditions [9–11].

To compensate for the shortcomings of onefold solid additive, core-shell structure additives with soft shell and hard core were constructed recently [12–15]. The core-shell structure can not only perform the deformation ability of the soft shell, but also play the bearing function of hard core. Meanwhile, core-shell microspheres as solid lubricant additive can achieve long life, low friction and good service reliability under harsh working conditions, due to their stable interfacial adhesion between soft shell and hard core [16]. Recently, MoS_2 as a metal dichalcogenide has been used as the “soft shell” of core-shell particles, to solve dispersion problems and enhance the mechanical and chemical stability of hard core [17–21]. Abdullah et al. [22] suggested that carbon spheres coated with a MoS_2 nanolayer (CS- MoS_2) demonstrated a significant reduction in friction and wear (15–35%) relative to standard engine oil in the boundary and mixed lubrication regimes. But MoS_2 as soft shell cannot react with the contact surfaces to

form robust tribo-film or reduce the surface roughness of the worn surface, which has a great negative impact on the tribological properties of core-shell microspheres [23]. Therefore, it is of great significance to find other soft materials to solve this problem.

Many investigations indicate that soft metal particles can act as friction modifiers [2]. Lubrication mechanisms of soft metallic nanoparticles could be explained by the sintering or repair effect, that is to say, the nanoparticles would be compacted on worn surface due to heat and pressure generated during friction process [24]. Although the soft metal has an excellent property in improving anti-wear performance, there are few researches regarding it as the soft shell of core-shell structure additives. Cu nanoparticles as a type of soft metal are often used as lubrication additives because of their good self-repairing property. Wang et al. [25] reported that the tribological performance of carbon nanotubes in base oil was improved via decorating with uniform copper nanoparticles. Qu et al. [26] demonstrated the good tribological properties of PTFE particles modified by Cu microparticles, because of the as-formed transfer film and self-repairing effect of Cu microparticles. Therefore, Cu is expected to be a kind of soft material to make up for the deficiency of MoS₂ as the shell of core-shell structure additives. However, the previous researches mainly used copper as a decoration, while the tribological performance of core-shell microspheres using Cu as the soft shell was rarely studied. Moreover, SiO₂ microspheres can be used to enhance the tribological properties of base oil [27, 28]. Due to its rigid structure and perfect spherical morphology, SiO₂ microspheres are often used as the hard core of core-shell structure additives [29–32]. Unfortunately, the tribological performance of SiO₂@Cu and SiO₂@MoS₂ as lubricant additives were rarely studied. As mentioned earlier, of great significance is to find preferable soft material to enhance the tribological properties of core-shell microspheres. Therefore, it is necessary to investigate the tribological properties of core-shell structural SiO₂@Cu and SiO₂@MoS₂ microspheres.

Overall, this paper aims to explore the lubrication effect and mechanism of Cu and MoS₂ as the soft shell of SiO₂ microspheres. In this work, SiO₂@Cu and SiO₂@MoS₂ core-shell microspheres were successfully synthesized, and were added into polyalphaolefin 40 (PAO 40) to study their lubrication function under different loads. For comparison, the tribological properties of single SiO₂, Cu and MoS₂ particles were also studied. In addition, the morphology of wear track and core-shell microspheres after test were investigated to reveal the anti-wear mechanism.

Experimental Details

2.1 Materials

All solvents and chemicals used in this work were analytical grades, purchased from Chengdu Kelong Chemical Co., Ltd. (Chengdu, China). SiO₂ NPs, with single-particle sizes ranging from 560 to 700 nm, were used in this study. The base oil, polyalphaolefin 40 (PAO 40) was obtained from Liugong Machinery Co., Ltd. (Guangxi, China), whose specification is shown in Table 1.

Table 1
Physical and chemical properties of base oil.

Base oil	Viscosity at 40°C (mm ² /s)	Viscosity at 100°C (mm ² /s)	Viscosity index (VI)	Pour point (°C)	Flash point (°C)
PAO 40	388.44	48.81	186	-42	280

2.2 Fabrication of SiO₂@Cu and SiO₂@MoS₂ microspheres

The synthesis route of the SiO₂@Cu and SiO₂@MoS₂ microspheres was illustrated in Fig. 1. As described in Fig. 1, a typical synthesis procedure of the SiO₂@Cu microspheres was as follows [20]. Firstly, 0.075 g SiO₂ was dispersed into 30 mL deionized water with sonication (KS-600 N, 250W) for 10 min to ensure uniform dispersion, 0.1 g anhydrous copper sulfate was added to 6.25 ml deionized water, then clear and transparent blue solution was formed by stirring with a glass rod. Secondly, the above solution was mixed and stirred with a magnetic stirrer for 30 minutes to ensure that the copper ions in the solution were in full contact with the surface of the silica. Then adding 0.035 g iron powders were slowly added at room temperature and reacting for 2 hours, the iron powders can be used as a reducing agent to reduce copper ions adsorbed on the surface of silica to copper. Lastly, the brown-red precipitation was collected by centrifugation and washed with distilled water and absolute ethanol until the excess reactants were removed.

In addition, the SiO₂@MoS₂ microspheres were synthesized by the following steps [32]. Firstly, 0.13 g SiO₂ was dispersed into 27 ml deionized water and mechanically stirred with ultrasonication. Secondly, 0.53 g sodium molybdate and 1.06 g thiourea were added and stirred with a magneton agitator for 1 hour. Then the mixed solution was transferred into a 100 ml Teflon-lined stainless-steel autoclave and heated at 200 °C for 10 h. After that, the autoclave was cooled to room temperature naturally. Finally, the black products were collected through centrifugation and washed with deionized water and ethanol several times, then dried at 60 °C for 12 h. The preparation method of MoS₂ is as the same as the above method, but the preparation process does not add SiO₂.

2.3 Characterization

The morphology of the as-obtained samples and friction surface were studied by using of a field-emission scanning electron microscope (SEM, FEI, Inspect F50, America) with an energy dispersive X-ray spectroscopic (EDS, acceleration voltage: 20 kV) detector. Raman spectra of wear tracks were obtained by Thermo-Fisher Scientific DXR Raman microscope with 532 nm laser excitation. Bruker Contour GT surface mapping microscope profilometer was used to examine the profile and wear volume of worn surfaces. An optical microscope (Zeiss Observer Z1m) was used to measure the wear track width and the wear scar diameter.

2.4 Tribological tests

PAO 40 was used as the lubricating fluid, and SiO₂@Cu, SiO₂@MoS₂, SiO₂, Cu and MoS₂ microspheres served as lubricating additives throughout this study. The as-prepared microspheres were added into the base oil with 1.0 wt.%. To make microspheres well dispersed in the base oil, the core-shell material was stably dispersed in the base oil through ultrasound for 2 h. The tribological properties of as-prepared lubricants were investigated using a ball-on-plate tribometer (Optimal-SRV-IV reciprocation friction tester) at different applied loads (20 ~ 200 N) for 1 h with the frequency of 2 Hz and displacement amplitude of 5 mm. The experiments were conducted at room temperature, with relative humidity between 55% and 70%. Before tribological tests, the steel ball and disk were thoroughly cleaned with ethanol and acetone. The GCr 15 bearing steel with a diameter of 10 mm was used as the upper specimen and the counterpart disk was composed of AISI 52100 steel with a size of 24×7.9 mm. As a contrast, the tribological properties of pure base oil were tested under the same conditions.

The average Hertzian contact pressure at 20 ~ 200 N was calculated with Hertz's theory [33]:

$$p = \frac{4W}{\pi a^2} \quad (1)$$

$$a = 2 \left(\frac{2}{3} * \frac{WR}{E'} \right) \quad (2)$$

Where, p is the Hertz contact pressure; a is the Hertz contact diameter; W is the normal load; R is the radius of steel ball ($R = 5$ mm); and E' is the effective modulus of elasticity ($E' = 208$ GPa). Calculated from the formula above, the corresponding contact pressures at 20~200 N are 1.264~2.724 GPa.

The boundary lubrication is especially significant for the form of tribo-film. Therefore, in order to compare the quality of the lubrication film formed by core-shell additives under different lubrication conditions, the corresponding lubrication conditions should be first determined according to the λ ratio in Equation (3). Where, h_{min} refers to the minimum film thickness and is evaluated by Equation (4), and R_q is the composite roughness calculated by Equation (5).

$$\lambda = \frac{h_{min}}{R_q} \quad (3)$$

$$h_{min} = 2.65R(\alpha E')^{0.54} \left(\frac{\eta_0 U}{E' R} \right)^{0.7} \left(\frac{W}{E' R^2} \right)^{-0.13} \quad (4)$$

$$R_q = \sqrt{R_{ball}^2 + R_{flat}^2} \quad (5)$$

Where, W is the applied load, R is the radius of the ball (5 mm), α is the viscosity–pressure coefficient (3.59×10^{-8} m²/N) U is the speed (0.01 m/s), η_0 is the dynamic viscosity (357 N•s/m²), R_{ball} is the surface roughness of the ball (79 nm), R_{flat} is the roughness of the flat (27 nm) and E' is elastic modulus (208 GPa). Usually, the value of λ is used to determine the lubrication regime: $0.1 < \lambda < 1$ indicates boundary

lubrication; $1 \leq \lambda \leq 3$ indicates mixed lubrication, and $\lambda > 3$ indicates elastohydrodynamic lubrication[23, 34, 35]. Using the corresponding values of the fundamental constants of physics and material characteristics, the lambda ratio is 0.973 for 200 N, 1.065 for 100 N, and 1.199 for 40 N. Therefore, the tests under 200 N were in the boundary lubrication regime, and under 40~100 N were in mixed lubrication regime.

After tests, the ball and disk samples were cleaned with ethanol, then placed in a sealed bag for later characterization tests. Each oil was tested three times, and the standard deviation was calculated from the results of the three times friction tests. To illustrate the role of the two types of core-shell microspheres in tribo-tests, the microspheres in the oil were collected with cotton after the friction test and washed with petroleum ether, then observed by SEM.

Results And Discussion

3.1 Characterization of the core-shell materials

SEM images of neat SiO₂, SiO₂@Cu and SiO₂@MoS₂ nanocomposites at different magnifications were shown in Fig. 2. The morphology of SiO₂ spheres was shown in Fig. 2a-b, it can be seen that SiO₂ spheres possessed a perfectly spherical structure, and the average diameter was about 623 nm according to the measurement results (Fig. 2c-d). The average diameter of SiO₂@Cu microspheres was about 694 nm. Apparently, copper nanoparticles were uniformly coated on the surface of SiO₂ spheres, forming a uniform copper shell layer with a thickness of about 35.5 nm. Likewise, as shown in Fig. 2e-f, SiO₂ spheres were surround by an irregular MoS₂-nanolayer. The results show that the average diameter of SiO₂@MoS₂ microspheres was about 683 nm, and the thickness of MoS₂-nanolayer was about 30 nm. It is worth noting that the MoS₂ shell prepared by the hydrothermal method do not exhibit traditional floral crystal structure but an amorphous structure, which can be attributed to magnetic stirring during the synthesis process [13]. Consequently, the differences in morphology and shell thickness between the two kinds of core-shell particles were basically eliminated, which was beneficial to compare lubrication performances between Cu shell and MoS₂ shell [17].

In order to further prove that the materials adsorbed on the surface of SiO₂ in the above figures are Cu and MoS₂, the surface elemental compositions of spherical particles were analyzed by EDS. As can be seen from Fig. 3a, Si, O and Cu elements were detected, and the peak value of each element was strong. Combined with the SEM image, it can be concluded that SiO₂@Cu core-shell structure composites were successfully synthesized. Similarly, the characteristic peaks of Si, O, Mo and S elements were detected in the microspheres from Fig. 3b, which fully demonstrated that SiO₂@MoS₂ nanocomposites were successfully synthesized.

Homogeneous dispersion plays a vital role in lubrication. Visual observations were used to determine the qualitative dispersion stability of the core-shell microspheres in PAO 40. As shown in Fig. 3c-d, the 1.0

wt.% $\text{SiO}_2\text{@Cu}$ and 1.0 wt.% $\text{SiO}_2\text{@MoS}_2$ nanospheres could be uniformly dispersed in oil after sonication. The oil containing $\text{SiO}_2\text{@Cu}$ appeared to be brownish-yellow in color, and the oil containing $\text{SiO}_2\text{@MoS}_2$ was black. After seven days of storage, the two core-shell microspheres still exhibited admirable dispersity, which could be due to their small size and the presence of oxygen-containing groups on their surface [26, 32, 36]. These results show that these nanoparticles have good dispersive stability, and can meet the requirements of the friction test.

3.2 Tribological behavior

The friction coefficient curves and average friction coefficient of SiO_2 , Cu and $\text{SiO}_2\text{@Cu}$ core-shell microparticles as lubricating additives under mixed lubrication regimes are shown in Fig. 4. Clearly, the friction curve of PAO 40 lubricating oil was relatively unstable, and even fluctuates wildly under 40 N and 60 N loads. The friction coefficient of submicron particles with SiO_2 compound lubricating oil was relatively stable, which could be due to the high bearing capacity of SiO_2 microspheres. However, the friction coefficient of SiO_2 increases gradually with the prolonging of experiment time, which was because the silica particles gradually gather during the friction process and cause serious abrasive wear. In addition, when $\text{SiO}_2\text{@Cu}$ core-shell microparticles as additives, the friction coefficient was not only lower than pure oil, but also very stable. In contrast, the overall friction curve of the lubricating oil with copper as an additive was smoother, and the average friction coefficient was lower than $\text{SiO}_2\text{@Cu}$. Obviously, SiO_2 microparticles cannot effectively reduce the wear under mixed lubrication conditions, but the copper layer wrapped in the outer layer of $\text{SiO}_2\text{@Cu}$ core-shell microspheres can make the friction coefficient tend to lower and more stable.

The tribological properties of MoS_2 , $\text{SiO}_2\text{@MoS}_2$ core-shell composite lubricants under mixed lubrication regime were also investigated. As can be seen from Fig. 5, MoS_2 performed well under low load conditions, with the lowest friction coefficient. But its friction coefficient continues to rise with the increase of load, which was closely related to the characteristics of soft texture and low bearing capacity of MoS_2 . The friction coefficient of $\text{SiO}_2\text{@MoS}_2$ core-shell microparticles was much lower than that of SiO_2 , indicating that soft shell was beneficial to reduce abrasive wear caused by hard particles. Unfortunately, the friction reduction effect of the $\text{SiO}_2\text{@MoS}_2$ core-shell microspheres as lubrication additives was not better than onefold materials, which maybe because it is difficult for core-shell particles to form stable tribo-film in the mixed lubrication state [17, 36].

By comparing the size of wear tracks and scars generated at 40 N (Fig. 6), it is found that using Cu and MoS_2 as soft shells could effectively reduce the wear caused by SiO_2 microspheres under a mixed lubrication regime. Especially, when $\text{SiO}_2\text{@Cu}$ spheres were used as lubricating additives, the wear scar diameter decreased 9.1% comparing with SiO_2 . In addition, when Cu or MoS_2 particles were used as lubricating additives, its tribological properties of them were better than core-shell particles. This may be due to the competitive mechanism of the abrasive wear of SiO_2 and the self-repairing property of soft

shells. Specifically speaking, the self-repairing property of Cu was better than that of MoS₂ according to the comparison of the wear scar diameter of SiO₂@Cu and SiO₂@MoS₂.

Figure 7 shows the friction coefficient curves and wear volume of the substrates lubricated by different oil samples at 100 N and 200 N. The friction experiments were still under mixed lubrication conditions at 100 N, so the friction coefficient and wear of the hybrid oil with various solid additives are greater than that of the pure oil. But the wear volume of SiO₂@Cu hybrid oil was still less than that of SiO₂@MoS₂, which was consistent with the results in Fig. 6. By contrast, SiO₂@Cu and SiO₂@MoS₂ core-shell materials as lubrication additives have obvious anti-wear and anti-friction effects under boundary lubrication regimes (200 N). Compared with pure oil, the friction coefficient of SiO₂@Cu and SiO₂@MoS₂ was reduced by 32.47% and 30.98% respectively, and the wear volume is reduced by 67.86% and 52.24%, respectively. It was worth noting that the anti-wear effect of the core-shell materials is better than that of any onefold additives (Fig. 7d). Under boundary lubrication regime, the wear resistance of Cu microspheres and MoS₂ was very poor when they were used as single solid lubrication additive, even the wear volume of MoS₂ was much larger than that of pure oil. This may be because the insufficient carrying capacity of these soft particles causes the oil film to rupture, then causing adhesive wear under high contact pressure and high friction heat. In addition, the wear volume of SiO₂@Cu and SiO₂@MoS₂ decreased by 48.45% and 23.39% compared with SiO₂, which indicates that the Cu shell has better wear reduction properties than SiO₂. Especially, no matter SiO₂@Cu or SiO₂@MoS₂, the wear-resistance of them was better than onefold additive (SiO₂, Cu and MoS₂). Core-shell microspheres as solid lubricant additive can achieve low friction and good service reliability under harsh working conditions.

Figure 8 shows the 3D surface morphologies and cross-sectional profiles of the wear track at 200 N lubricated with PAO 40, SiO₂, SiO₂@Cu and SiO₂@MoS₂ hybrid oil. From Fig. 8a we can see the cross-sectional profile from PAO 40 lubrication displays maximum wear track depth (1.364 μm), which could be attributed to contact fatigue and adhesive fatigue during the tribo-test. Whereas, the deep of wear track was decreased to 1.127 μm when 1 wt.% SiO₂ microspheres were added to the pure oil, suggesting that the SiO₂ microspheres filled the gaps in the worn surface and was beneficial for reducing wear. By contrast, the wear track depth of lubricant with SiO₂@Cu and SiO₂@MoS₂ microspheres was reduced to 0.752 μm and 0.748 μm, respectively. Consequently, those results indicated that the soft shell of core-shell structure microspheres improves the anti-wear properties of SiO₂. which were consistent with the change of friction coefficient and wear volume mentioned above.

3.3 Analysis of worn surface

After the friction test, we observed the wear tracks and wear scar morphology by optical microscope, then analyzed the EDS element diagram under mixed lubrication conditions (40 N). As can be seen from Fig. 9a, there are a lot of furrows on the PAO 40 lubricated worn surface, the width of the wear tracks reaches the maximum of 228 μm, which indicated that the poor bearing capacity of pure lubricating oil leads to seriously wear on the contact surface. Figure 9f shows that EDS detected Si element signal,

which indicated SiO_2 particles were adsorbed on the surface of the wear track. There are obviously deeper furrows on the wear surface of SiO_2 lubricating oil (Fig. 9b), due to the three-body abrasion of SiO_2 microparticles, which have high hardness and brittle texture. Moreover, it can be seen from Fig. 9c-d that $\text{SiO}_2@\text{Cu}$ and $\text{SiO}_2@\text{MoS}_2$ core-shell materials hybrid lubricating oils have a lower wear track width than SiO_2 , and obvious black-brown transfer film was generated on the wear mark. EDS detected Cu and S element signal at their wear tracks even though the content of these elements was relatively low (Fig. 9g-h), which indicates that the synergistic effect of SiO_2 and Cu or MoS_2 plays a role in the friction process. Additionally, compared to the conditions which were lubricated with SiO_2 hybrid oil, the wear scar diameter was smaller when lubricated by $\text{SiO}_2@\text{Cu}$ hybrid oil, while the wear scar diameter of $\text{SiO}_2@\text{MoS}_2$ was almost same as SiO_2 . Hence, the abrasive wear reduction of Cu shell under mixed lubrication conditions was better than MoS_2 .

Moreover, the worn surface after sliding for 1 h at 200 N was characterized by SEM and EDS (Fig. 10), the results can be used to analyze the effect of different additives under boundary lubrication conditions. The SEM results were basically consistent with the 3D morphology (Fig. 8). As shown in Fig. 10a, when pure oil was used for lubrication, there are large spalling pits and O element (14.95 wt.%) on the wear marks. That is because pure oil cannot reduce high contact pressure and interfacial flash temperature effectively, leading to serious adhesive wear and oxidation on the worn surface. Interestingly, when SiO_2 microspheres were added, spalling pits on the worn surface were fewer, but deep furrows were produced by abrasive wear (Fig. 10b). EDS analysis shows that Si (0.69 wt.%) and O (11.10 wt.%) elements exist on the wear track, indicating the particles can be transferred and deposited on the worn surface. There are reasons to believe that SiO_2 microparticles could improve the anti-wear ability of base oil to a certain extent under boundary lubrication conditions, but will cause abrasive wear, because it is difficult to produce stable tribo-film [27]. Figure 10c-d show the morphology of the worn surface when $\text{SiO}_2@\text{Cu}$ and $\text{SiO}_2@\text{MoS}_2$ microspheres were added, respectively. As we can see, the worn surfaces lubricated by soft-shell@hard-core microparticles all display shallower and smoother wear tracks. Even more importantly, the friction contact surface was the smoothest when $\text{SiO}_2@\text{Cu}$ particles were added, and covered with a stable and robust tribo-film which containing a large amount of copper (37.13%). On the contrary, the wear track of $\text{SiO}_2@\text{MoS}_2$ hybrid oil exhibited deeper furrows and fewer Mo element (16.29 wt.%), suggesting that the tribological transfer film formed by the MoS_2 shell was weaker than Cu shell. It implies that using Cu as shells are better than MoS_2 in the self-repairing property. On the other hand, the ratio of O element in $\text{SiO}_2@\text{Cu}$ lubricated surface decreased sharply than SiO_2 hybrid oil, this is due to that the core-shell particles can promote the formation of a compact tribo-film in the contact area, which is conducive to preventing oxidation of the worn surface [37]. Thus, soft-shell@hard-core microparticles were proved to be an admirable composite material with better self-repairing property, and Cu as soft shells are likely better than MoS_2 for protecting contact surfaces [18].

Furthermore, in order to study the properties of the tribo-film formed by $\text{SiO}_2@\text{MoS}_2$ microspheres hybrid oil, the worn surfaces at 200 N are investigated by Raman spectra analysis as shown in Fig. 11.

According to the Raman spectrum, peaks at 223, 295, 411 and 663 cm^{-1} (Fig. 11a) can be assigned to the spectra of Fe_2O_3 and Fe_3O_4 [38], which indicated that there is a large amount of iron oxide on the worn surfaces. In fact, the occurrence of oxidative wear is one of the reasons for the poor anti-wear effect of pure oil under boundary conditions [39]. In Fig. 11b, two weak peaks at 373 and 410 cm^{-1} (E_{2g}^1 and A_{1g} mode) of MoS_2 were discovered on the wear traces tested by $\text{SiO}_2@\text{MoS}_2$ hybrid oil, indicating that the $\text{SiO}_2@\text{MoS}_2$ microspheres in base oil could enter the friction surfaces to form the tribo-film on the contact areas [40]. However, the intensity of E_{2g}^1 and A_{1g} mode peaks were relatively low, this could be due to the weak reaction with the worn surfaces [41, 42]. Besides, peaks at 292 and 670 cm^{-1} also can be assigned to the spectra of different iron oxides, the absence of peaks at 223 and 411 cm^{-1} may be because the decrease of oxidative wear [8]. As the main component of the tribo-film, iron oxides and MoS_2 play a vital role in boundary lubrication. Eventually, the analysis results of Raman spectra show that the soft-shell@hard-core microparticles were beneficial to the reduction of oxidative wear, but MoS_2 as the soft shell of SiO_2 cannot give aid to the formation of the robust tribo-film during the frictional process [43].

3.4 Lubrication mechanism

The topographies of microspheres are related to the lubrication mechanism and follow a certain evolution law, which provides an effective weapon for us to study the effect of core-shell particles on different lubrication regimes. Therefore, the morphology and microstructure of $\text{SiO}_2@\text{Cu}$ and $\text{SiO}_2@\text{MoS}_2$ microparticles after the test could shed more insight into the lubrication mechanism. As shown in Fig. 12a-b, most the microspheres maintain original morphology after friction test at low contact pressure (1.593 GPa) for 1 h, and only a few of the $\text{SiO}_2@\text{Cu}$ and $\text{SiO}_2@\text{MoS}_2$ microspheres were broken. The spherical structure of the crushed core-shell microspheres was deformed into irregular spheres. Moreover, EDS results in Fig. 12a-b show that Cu and MoS_2 still exist on the surface of the SiO_2 particles, demonstrating that the part of the shell has not worn completely during the friction. Correspondingly, the morphology and EDS analysis of $\text{SiO}_2@\text{Cu}$ and $\text{SiO}_2@\text{MoS}_2$ spheres after tribo-tests at 200 N for 1 h were shown in Fig. 12c-d, respectively. We can see clearly that original $\text{SiO}_2@\text{Cu}$ and $\text{SiO}_2@\text{MoS}_2$ spheres were crushed into smaller spheres at high contact pressure (2.724 GPa). Surprisingly, EDS results show that the surface of the crushed particles did not contain Cu or MoS_2 , indicating the particles suffered serious wear, leading to the exposure of internal SiO_2 core part. By observing the change of particle morphology after test under different loads, we found that whether $\text{SiO}_2@\text{Cu}$ or $\text{SiO}_2@\text{MoS}_2$ particles, low pressure could make the surface of the spheres become rough, while high pressure could make the particles completely broken and the shell peeled off [43]. The breaking degree of $\text{SiO}_2@\text{Cu}$ microspheres was lower after the friction experiment, demonstrating that soft metal shell can equip the microspheres with a higher load-carrying capacity. Under boundary lubrication, using microparticles of soft-shell and rigid-core as lubricant additives can not only take advantage of the easy formation of a transfer film, but also bring the advantages of small size and bearing advantage of the hard nanoparticles into full play

[38]. The two-phase composite particles were gradually peeled off during the rolling process, which promote the uniformity and integrity of the transfer film and enhance the self-healing capacity [14].

Combining with the analysis of the worn surface and microparticles after the test, the lubrication mechanism of two kinds of soft-shell@hard-core microspheres under different lubrication regimes was deduced, as depicted in Fig. 13. To begin with, the molecules of lubricant and core-shell microspheres were adsorbed on the frictional interfaces and formed a tribo-film during the friction process. During mixed lubrication conditions, the core-shell microspheres were acted as ball-bearings on the nanometer scale, and only a few particles enter the worn surface to act as a third body material filling the gap on the worn surface [16]. The surface of the particles which have entered the contact area would be slightly deformed. Meanwhile, the core-shell microspheres were sheared off on the worn surface due to the role of shear force, and a weak physical tribo-film was formed at the same time [2]. By contrast, during boundary lubrication conditions, the contact between the microbulges leads to the oil film piercing. Then core-shell particles broken up completely into smaller spheres and the shell of those particles peeled off under high load. Besides, the debris formed by the wear and core-shell particles would fill the pits on the worn surface to repair the damaged region and reduce the surface roughness. At the same time, for $\text{SiO}_2\text{@Cu}$ hybrid oil, microspheres gradually deposit to the friction interface during the friction process, then Cu shell become melt and spread to form a dense protective film under high temperature and pressure, and repair the damaged interface [37]. Then the crushed SiO_2 turn into a carrier to support worn surface [19], and form a composite boundary lubrication film with Cu shell [44]. For $\text{SiO}_2\text{@MoS}_2$ hybrid oil, the thermal induction during sliding can increase the size and crystallinity of MoS_2 , and the parallel sliding of MoS_2 along the section induced by high pressure was beneficial to reduce the friction. However, the peeled MoS_2 nanosheet cannot form a stable adsorbed film and a robust tribo-film, that is the reason why the tribological properties of $\text{SiO}_2\text{@MoS}_2$ were worse than that of $\text{SiO}_2\text{@Cu}$. On the whole, the physical deposition of core-shell microparticles, self-repairing of the Cu shell, and chemical reaction of base oil together construct a synergistic effect, which can contribute to the optimal lubrication performance of $\text{SiO}_2\text{@Cu}$.

Conclusions

In this work, $\text{SiO}_2\text{@Cu}$ and $\text{SiO}_2\text{@MoS}_2$ microspheres were synthesized to explore the lubrication properties and corresponding mechanism of Cu and MoS_2 as the soft shell of SiO_2 microspheres. Friction experiments were carried out at different loads, then the morphologies and elementary compositions of worn surface and wear debris were investigated to reveal the lubrication mechanism of $\text{SiO}_2\text{@Cu}$ and $\text{SiO}_2\text{@MoS}_2$ microspheres. The following conclusions can be drawn from this work:

(1) $\text{SiO}_2\text{@Cu}$ and $\text{SiO}_2\text{@MoS}_2$ core-shell microspheres were prepared by iron reduction process and hydrothermal method. The core diameter and shell thickness were about 623 nm and 30 nm, respectively.

(2) Core-shell structure hybrid oils display excellent friction-reduction and wear-resistance at high applied loads. The lubrication behaviors of $\text{SiO}_2@\text{Cu}$ are superior to that of $\text{SiO}_2@\text{MoS}_2$ (the addition of 1.0 wt.% $\text{SiO}_2@\text{Cu}$ and $\text{SiO}_2@\text{MoS}_2$ can reduce wear volume by 48.45% and 23.39% with SiO_2 as a comparison).

(3) Rolling effect of SiO_2 , easy-shearing and self-repairing of Cu shell together construct a synergistic effect, thereby contributing to optimal lubrication performance of $\text{SiO}_2@\text{Cu}$.

Declarations

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Figures

Figure 1

Synthetic procedures for preparation of the SiO₂@Cu and SiO₂@MoS₂ microspheres

Figure 2

SEM micrographs with low and high magnification of microspheres: a-b SiO_2 , c-d $\text{SiO}_2@\text{Cu}$, e-f $\text{SiO}_2@\text{MoS}_2$

Figure 3

EDS analysis results of core-shell microspheres: a SiO₂@Cu, and b SiO₂@MoS₂. Dispersion properties of 1.0 wt.% microspheres in PAO 40: c SiO₂@Cu microspheres, and d SiO₂@MoS₂

Figure 4

The friction coefficient curves and the average friction coefficient lubricated by oils with different copper related additives: a-b at 20 N, c-d at 40 N, and e-f at 60 N

Figure 5

The friction coefficient curves and the average friction coefficient lubricated by oils with different molybdenum disulfide related additives: a-b at 20 N, c-d at 40 N, and e-f at 60 N

Figure 6

Wear scar diameter lubricated by PAO, SiO₂, Cu, MoS₂, SiO₂@Cu and SiO₂@MoS₂ at 40N

Figure 7

Friction coefficient and wear volume under 100 N and 200 N

Figure 8

3D profile and 2D depth profile of the wear tracks at an applied load of 200 N: a PAO 40, b SiO₂, c SiO₂@Cu, and d SiO₂@MoS₂

Figure 9

Optical images and EDS spectra of wear tracks at 40 N: a, e PAO 40, b, f SiO₂, c, g SiO₂@Cu, and d, h SiO₂@MoS₂

Figure 10

SEM and EDS analysis of wear tracks at 200 N, lubricated with a PAO, b SiO₂, c SiO₂@Cu, and d SiO₂@MoS₂, respectively

Figure 11

Raman spectra of worn surface at 200 N: a PAO, and b SiO₂@MoS₂

Figure 12

SEM images and EDS spectra of friction products at 40N and 200N: a and c SiO₂@Cu, b and d SiO₂@MoS₂

Figure 13

Schematic of lubricating mechanism of additives

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