



Study of low-toxicity copper pyrithione as a multifunctional additive for lithium grease



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ABSTRACT

The feasibility of CuP as a multifunctional additive in lithium grease was evaluated for the first time. The experimental results indicated that the CuP significantly enhanced the friction reduction, antiwear properties, extreme pressure capabilities, and antimicrobial characteristics of lithium greases. The SRV test results suggested that the optimal tribological properties were obtained by adding 3 wt% of CuP to lithium greases, resulting in a decrease of the friction coefficient and wear volume by 28.25% and 34.98%, respectively. The four-ball results confirmed that the extreme pressure performance of the lithium grease with 3 wt% CuP was enhanced by a factor of 3.17. The bacterial inhibition rate of lithium grease with 3 wt% CuP was higher than 99.98%. The lubrication mechanism and antimicrobial mechanism was explained.

1. Introduction

Lubricants are widely used in machinery and equipment, where they play important roles in reducing friction and wear, prolonging the service life of equipment and reducing energy consumption by the moving parts [1–4]. Additives are important components of lubricants and are essential for enhancing and imparting special properties to the lubricants. Additives significantly improve the tribological properties of the lubricants and enhance their oxidation resistance, rust resistance, etc. [5–7]. Currently, additives are predominantly categorized as friction reduction additives, antiwear additives, extreme pressure additives, antioxidants, rust inhibitors, and antimicrobial agents [8]. The majority of additives currently in use are singular function additives. The need to incorporate multiple additives to obtain a lubricant with excellent performance has resulted in the use of many additives in large quantities. However, as environmental regulations intensify, there is an inevitable trend toward minimizing the quantity of additives employed [9]. Furthermore, the diverse molecular structures and distinct mechanisms of action exhibited by various additives lead to countersynergistic effects [10]. Lubricant formulation researchers must conduct many experiments to optimize both the types and ratios of additives, a process that often results in inefficient lubricant development. The introduction

of multifunctional additives presents a promising solution to these challenges.

Some progress has been made in the research on multifunctional additives. The main focus has been on the study of multifunctional additives that improve lubricant viscosity, friction reduction and antiwear properties, extreme pressure properties and oxidation resistance. The viscosity and antiwear properties of lubricants were significantly enhanced by the preparation of complex polyacrylate-magnetite nanocomposites (PNCS), which were made from the Fe₃O₄-filled homopolymer of dodecyl acrylate [11]. Oil-soluble phosphates exhibited friction reductions and antiwear properties, extreme pressure capacity and rust protection in lubricants [12]. Imidazolium ILs in polyurea greases exhibited good antiwear and anticorrosion properties [13]. Jiao Wang et al. developed a multifunctional additive for mercaptotriazinyl organomolybdate that exhibited good friction reduction, antiwear properties and extreme pressure performance in ester oils [14].

Moreover, it is important to note that lubricants are susceptible to microbial activity during storage, transportation, and operation under unfavorable conditions such as high temperatures and humidity. The proliferation of microorganisms can lead to lubricant degradation, an increase in the acid value, alterations in color and odor, and a more corrosive nature [15,16]. Consequently, good antimicrobial properties

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Table 1
Physical properties of base oils.

Property	Base oils	Test Method
Kinematic viscosity (40 °C)/mm ² · s ⁻¹	216.5	GB/T 265
Kinematic viscosity (100 °C)/mm ² · s ⁻¹	22.8	GB/T 265
Viscosity index (VI)	129	GB/T 1995
Pour point/°C	-38	GB/T 3535
Flash point/°C	262	GB/T 267

Table 2
Physicochemical properties of the lithium greases.

Properties	Li	Li-1 wt%	Li-2 wt%	Li-3 wt%	Li-4 wt%	Test method
Worked penetration/mm	293	289	287	287	286	GB/T 269
Dropping point/°C	214	214	213	214	214	GB/T 3498
Oil separation (100 °C, 24 h)/%	2.21	2.08	1.91	1.70	1.36	NB/SH/T 0324

of lubricants are crucial for ensuring stable performance and longevity.

Research has demonstrated that S, Cu, and N compounds possess commendable tribological properties [17,18]. Copper pyridine (CuP), a compound comprising the elements S, Cu, and N, is recognized as a low-toxicity substance by the European BR. It has found extensive application in antifouling coatings and pharmaceuticals [19,20]. However, there is no research investigating the potential of copper pyridine as a multifunctional additive for lubricants.

Grease is a widely used lubricant, and lithium grease is one of the most commonly used types of grease. The potential of CuP as a multifunctional additive for lithium grease was studied in this paper. The tribological and antimicrobial properties of the grease samples were evaluated. The findings revealed that CuP demonstrated good friction reduction and antiwear characteristics, extreme pressure performance, and antimicrobial activity within lithium grease. The lubrication mechanism of CuP in lithium grease was elucidated with wear surface analyses. Additionally, the antimicrobial mechanism of CuP in grease was discussed.

2. Materials and methods

2.1. Materials

Cupric chloride dehydrate and 2-mercaptopurine-N-oxide were purchased from Macklin Biochemical Technology Co., Ltd. Methanol, NaOH and diethyl ether were obtained from Sinopharm Chemical Reagent Co., Ltd. Lithium grease was obtained from Qingdao Lubemate Lubrication Materials Technology Co., Ltd. The base oil of the lithium grease was polyalphaolefin. The viscosity of the base oil of physical properties are shown in Table 1. The water utilized in the study was distilled.

2.2. Synthesis of CuP

The synthesis of CuP was conducted via the method of Dasireddy et al. [21]. In detail, 2-mercaptopurine-N-oxide (280 mg) was dissolved in 30 ml of methanol and stirred thoroughly. A sodium hydroxide solution (1 mol/L) was then gradually introduced to this solution, after which the pH was adjusted to 8. Subsequently, cupric chloride dihydrate (188 mg) was added to the aforementioned mixture and stirred at 20 °C for an hour. The product was subsequently filtered under reduced pressure and washed three times with methanol, followed by three washes with diethyl ether. The resultant solid was subjected to freeze-drying for 24 h, yielding green CuP.

2.3. Fabrication of grease samples

The prepared CuP was added to lithium grease at a 1% mass fraction and then homogenized for 5 min with a mixer (Speedmixer, DAC515, Flack Tek) at 2500 rpm. The mixture was then ground three times with a precision three-roll mill (80E, Exakt). The lithium grease samples contained a 1% CuP mass fraction and were designated Li-1wt% CuP. In addition, lithium grease samples containing 2%, 3% and 4% Cu were prepared by the same method. These materials were named Li-2 wt%, Li-3 wt% and Li-4 wt%, respectively. The Physicochemical properties of the samples are shown in Table 2.

2.4. Characterizations and measurements

Fourier transform infrared (FTIR) spectra of CuP were obtained with an infrared spectrometer (Tensor 27, Bruker). The sample scanning range was 4000 to 500 cm⁻¹. X-ray photoelectron spectra (XPS) were recorded with an X-ray photoelectron spectrometer (K-Alpha, Thermo Scientific) with Al K monochromatic radiation. The binding energies were referenced to the C 1s peak at 284.8 eV for alkyl or indeterminate carbon. The chemical composition of the synthesized CuP was analyzed with XPS.

2.5. Tribological performance

An oscillating reciprocating tribometer (SRV-V, Optimol) was used to evaluate the friction reduction and antiwear properties of the grease samples. The test was performed with an SRV instrument using a steel test ball oscillating against a stationary steel test disk with the lubricant between them. The test balls (diameter: 10 mm, mean roughness: 25 nm, RC hardness: 62–65) and disks (diameter: 24 mm, thickness: 7.85 mm, mean roughness: 70 nm, RC hardness: 62–65) were made of 52100 standard steel. The SRV tests were conducted under the following conditions: a load of 100 N, an amplitude of 1 mm, and a frequency of 25 Hz. The test temperatures were 75 °C, 100 °C and 125 °C. The test durations were 30 min.

A four-ball tester (MS-10A, Tenkey) was utilized to assess the friction reduction, antiwear performance, and extreme pressure properties of the grease samples. The friction reduction and antiwear performance were evaluated in accordance with the Chinese petrochemical industry standard SH/T 0204-92. The testing conditions included a speed of 1200 rpm, a temperature of 75 °C, a load of 392 N, and a test duration of 60 min. In contrast, an extreme pressure performance assessment was conducted with the GB/T 3142-1982 standard method, with a test speed of 1450 rpm, room temperature, load variation, and a test duration of 10 s. The test ball was made from 52100 standard steel and exhibited a diameter of 12.7 mm and an RC hardness of 64–66, with a polish grade of 25. Each sample was tested three times to ensure reproducibility.

2.6. Analyses of worn surfaces

The wear volumes and cross-sectional profile curves of the wear scars on the test disks were measured with a noncontact 3D surface mapping profilometer (KLA-Tencor). The morphologies of the wear scars were characterized with a scanning electron microscope (SEM, JSM-7610F, JEOL) equipped with an energy dispersive spectrometer (EDS) attachment. The chemical compositions of the wear scar surfaces on the test disks were analyzed with XPS.

2.7. Antimicrobial performance testing

S. aureus was selected as the test strain. First, all utensils used in the experiment were sterilized. The solid medium was configured, sterilized in an autoclave, poured into a surface dish, cooled to form a solid under an ultraviolet sterilization lamp, and set aside. The preserved strains were transferred from the media to slant media with a sterile inoculation

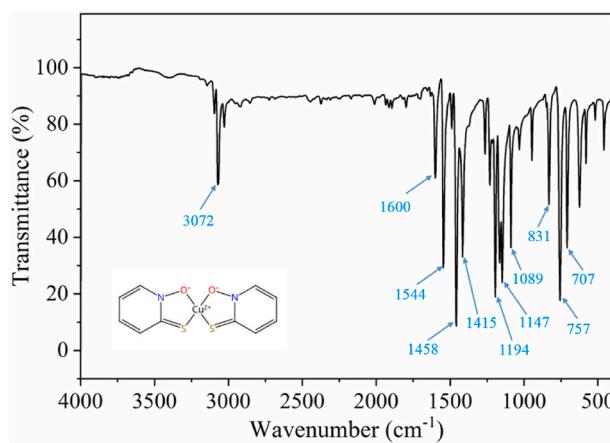


Fig. 1. FTIR spectrum of CuP.

ring and cultivated for 24 h at $35 \pm 1^\circ\text{C}$. The activated strains were placed in a glass test tube with liquid medium and incubated in a shaking incubator for 24 h. The original bacterial suspension was diluted into bacterial suspensions of different concentrations by the tenfold dilution method, and the numbers of bacteria corresponding to these bacterial suspensions were subsequently calculated by the plate colony counting method to select appropriate bacterial suspensions with concentrations of 10^8 CFU/mL for the experiment. A 1.50 mg sample of Li-3 wt% and the Li control sample were weighed and placed in a sterilized test tube with the bacterial solution added. Another test tube was prepared with the same amount of experimental bacterial solution added as a blank control. The test tube was incubated in an oscillating incubator for 24 h. The cultured bacterial solution was diluted with 9 g/L normal saline, and the dilution times were 10^2 , 10^3 and 10^4 , respectively. Then, 100 μL of the bacterial solution was added to the prepared solid medium with a straw and coated with 4 mm diameter glass beads. After the

surface was dry and not stained with water, the cells were cultured in an incubator for 18 h.

Finally, photos were taken to record the results. The following formula was used to calculate the inhibition rate [22]:

$$A = \frac{A_0 - A_i}{A_0} \times 100\%$$

where A is the bacterial inhibition rate of the sample and A_0 and A_i represent the numbers of colonies on the blank and experimental plates, respectively.

3. Results and discussion

3.1. Characterization of CuP

The infrared spectrum of CuP is depicted in Fig. 1. The peak at 3072 cm^{-1} corresponded to the C-H stretching vibrations of the pyridine ring. Other peaks observed at 1600 cm^{-1} , 1544 cm^{-1} , 1458 cm^{-1} , and 1415 cm^{-1} were attributed to stretching vibrations of the pyridine ring. Additionally, the peaks at 1194 cm^{-1} and 1089 cm^{-1} were resulted from a stretching vibration of the N-O bonds. The peak at 1147 cm^{-1} corresponded to the stretching vibration of the C=S bonds. Finally, the absorption peaks at 831 cm^{-1} , 757 cm^{-1} , and 707 cm^{-1} were attributed to the bending vibrations of the C-H bonds in the pyridine ring [21].

The structure of the CuP compound was characterized with XPS. Fig. 2 shows the high-resolution Cu 2p, S 2p, N 1s and O 1s XPS spectra. Two Cu 2p peaks appeared at binding energies of 952.7 eV (Cu 2p_{1/2}) and 932.6 eV (Cu 2p_{3/2}) in the high-resolution XPS spectrum of Cu. The peak near the binding energy of 952.5 eV was attributed to the Cu-S bond in CuP. The peak at 932.6 eV was attributed to the Cu-O bond in CuP [23]. The S 2p peaks appeared at 162.9 eV and 161.8 eV. These peaks were attributed to the S-Cu and S-C bonds of CuP, respectively [24]. The N 1s peak was deconvoluted into two main peaks located at binding energies of 402.3 eV and 399.9 eV, and were attributed to the

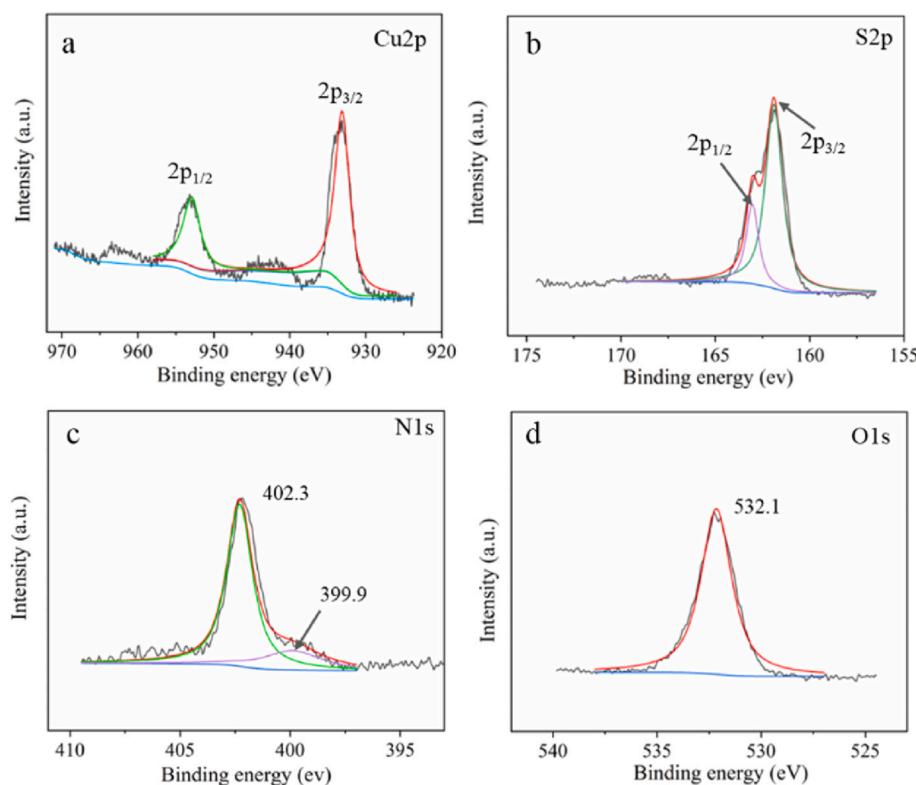


Fig. 2. XPS spectra of CuP; (a) Cu 2p, (b) S 2p, (c) N 1s and (d) O 1s binding energies.

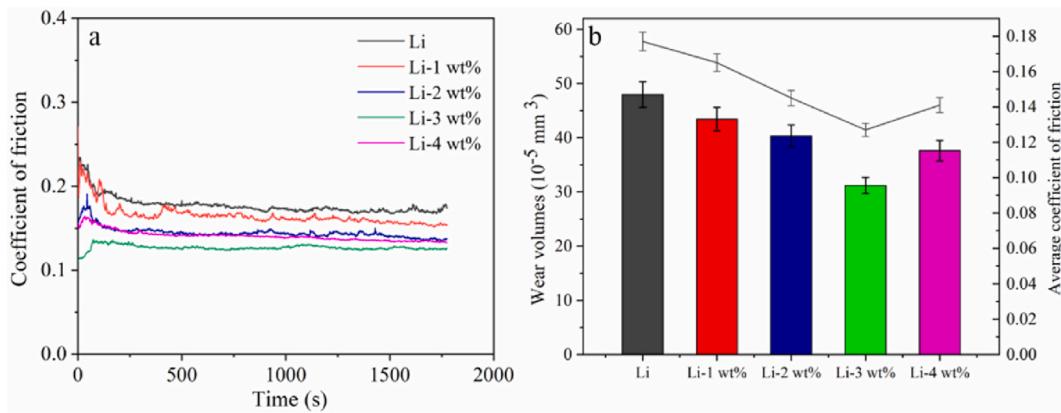


Fig. 3. Coefficients of friction (a) and wear volumes (b) versus the amount of CuP added to the lithium grease at 100 °C.

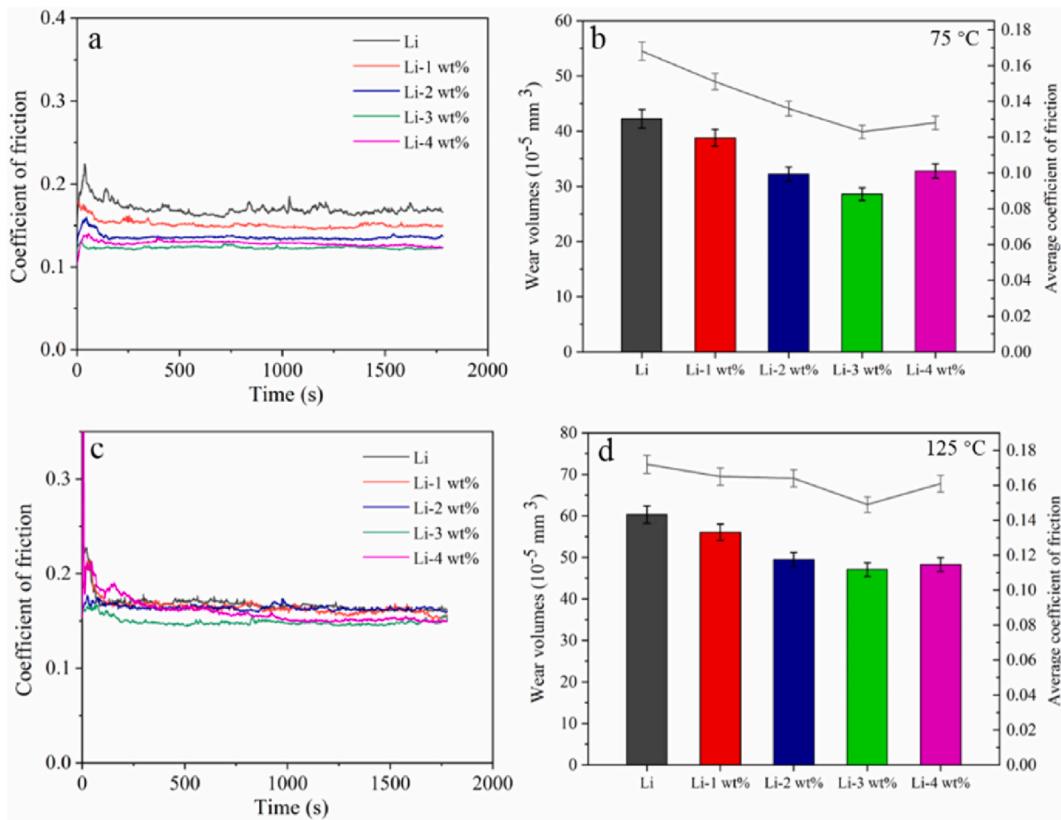


Fig. 4. Coefficient of friction and wear volume of lithium greases with different concentrations of CuP at 75 °C (a, b) and 125 °C (c, d).

N–O and N–C bonds, respectively. The O 1s peak was centered at a binding energy of 532.1 eV for metal oxides and nitrogen oxides [25]. These results indicated that CuP was successfully synthesized.

3.2. Tribological properties

The friction reduction and antiwear properties of the lithium grease with CuP were evaluated at 100 °C via SRV. Fig. 3 shows the coefficients of friction and wear volumes of lithium greases with different concentrations of CuP. The coefficient of friction of Li without added CuP was high. The coefficients of friction for the lithium greases with added CuP decreased. Compared with the coefficient of friction for Li, the coefficient of friction for lithium grease decreased gradually with increasing CuP addition, and the coefficient of friction for lithium grease was the lowest when the additive concentration was 3 wt%. The average friction

coefficient of Li-3 wt% was 28.25% lower than the average friction coefficient of Li. Thus, the addition of CuP significantly improved the friction reduction performance of the lithium grease. When the amount of CuP added was increased to 4 wt%, the coefficient of friction increased slightly. Moreover, Fig. 3(b) shows that the pattern of the wear volume of the grease samples was consistent with the coefficient of friction. The wear volume of lithium grease was the smallest when the concentration of added CuP was 3 wt%. Compared with that of Li, the wear volume of Li-3 wt% was 34.98% lower. These experimental results showed that CuP exhibited good friction reduction and antiwear properties at 100 °C, and the optimal level of addition in the lithium grease was 3 wt%.

In order to investigate the tribological properties of CuP in lithium grease at different temperatures, the tribological properties of lithium greases with different concentrations of CuP were evaluated at

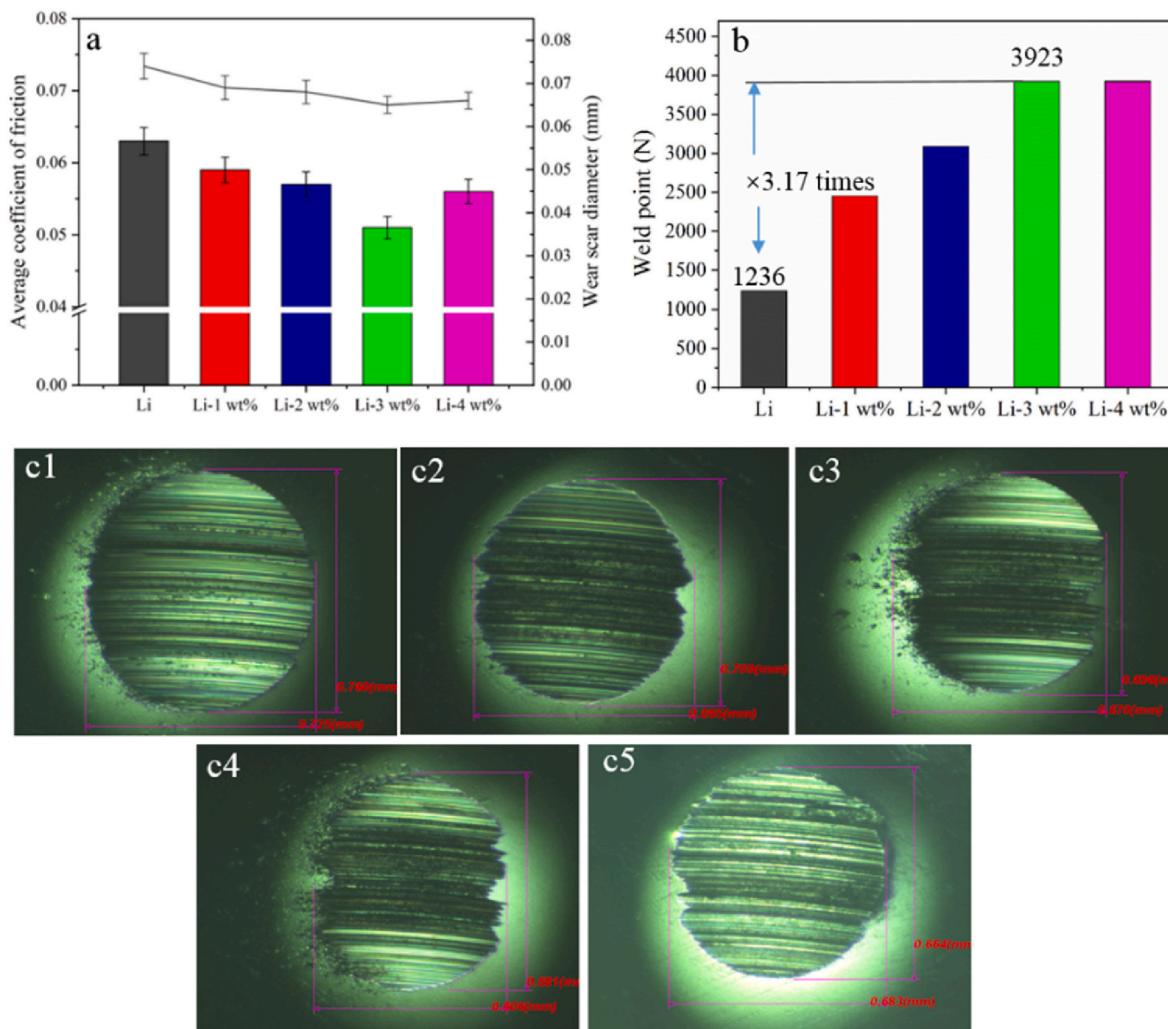


Fig. 5. Test results for amount of CuP added to the lithium grease from the four-ball tester. (a) Average coefficient of friction and wear scar diameters. (b) Weld point. (c1-c5) Image of a wear scar lubricated with Li, Li-1 wt%, Li-2 wt%, Li-3 wt%, and Li-4 wt%.

temperatures of 75 °C and 125 °C, as shown in Fig. 4. The variation law in the average coefficient of friction and wear volume, as a function of increasing CuP concentration for lithium grease samples at 75 °C and 125 °C, was consistent with that observed at 100 °C. The optimal level of addition in the lithium grease was 3 wt%. The coefficients of friction and wear volume for Li-3 wt% were observed to be lower than those of Li at the examined temperatures. CuP significantly improved the friction reduction and antiwear properties of lithium grease. Specifically, the average friction coefficient for Li-3 wt% decreased by 26.79% and 13.37% at 75 °C and 125 °C, respectively, relative to that of Li. Correspondingly, the wear volume for Li-3 wt% reduced by 32.38% and 21.95%, respectively. These findings suggested that CuP exhibited optimal friction reduction and antiwear properties at 100 °C. This performance could be attributed to the influence of temperature on the tribochemical reaction, leading to variations in the lubrication films.

To evaluate the improvement effect of CuP on the tribological properties of lithium grease, the friction reduction, antiwear and extreme pressure properties of lithium greases were tested with a four-ball tester. Li-3 wt% had the lowest average friction coefficient and the smallest wear scar diameter (Fig. 5 a). Fig. 5(a) shows that the average coefficient of friction and wear scar diameter for Li-3 wt% were 19.04% and 12.38%, respectively, lower than those of Li. The images showing the wear scar diameters (Fig. 5(c1-c5)) supported the test results of the wear scar diameter. Notably, the extreme pressure performance of Li-3 wt% was 3.17 times better than that of Li, as shown in Fig. 5(b).

These results implied that CuP significantly enhanced the extreme pressure performance of the lithium grease. Consequently, these findings showed that CuP exhibited good friction reduction, antiwear and extreme pressure capabilities in lithium grease.

3.3. Worn surface analyses

A 3D surface mapping profilometer was used to characterize the surface morphologies and depths of the wear scar cross-sections on the SRV test discs to determine wear in more detail. As shown in the surface morphology images in Fig. 6, all of the test discs lubricated with the grease samples had wear scars with multiple furrows. The wear scar for Li had rougher surfaces with more and deeper furrows, while the wear for Li-3 wt% had flatter surfaces with fewer and shallower furrows. A comparison of the cross-sectional depth profiles of the abrasion marks produced by the different grease samples showed that Li produced the deepest wear scar, with a maximum depth of approximately 2.75 μm, while Li-3 wt% produced the shallowest wear scar, with a maximum depth of approximately 1.4 μm. These test results also showed that CuP improved the antiwear capabilities of the lithium greases.

The surface morphologies of the wear scars were characterized with SEM. The morphologies of the wear scars on the test discs lubricated with lithium greases containing different concentrations of CuP are shown in Fig. 7. The wear scar from Li had the most and deepest furrows. The wear furrows from the lithium greases containing CuP became

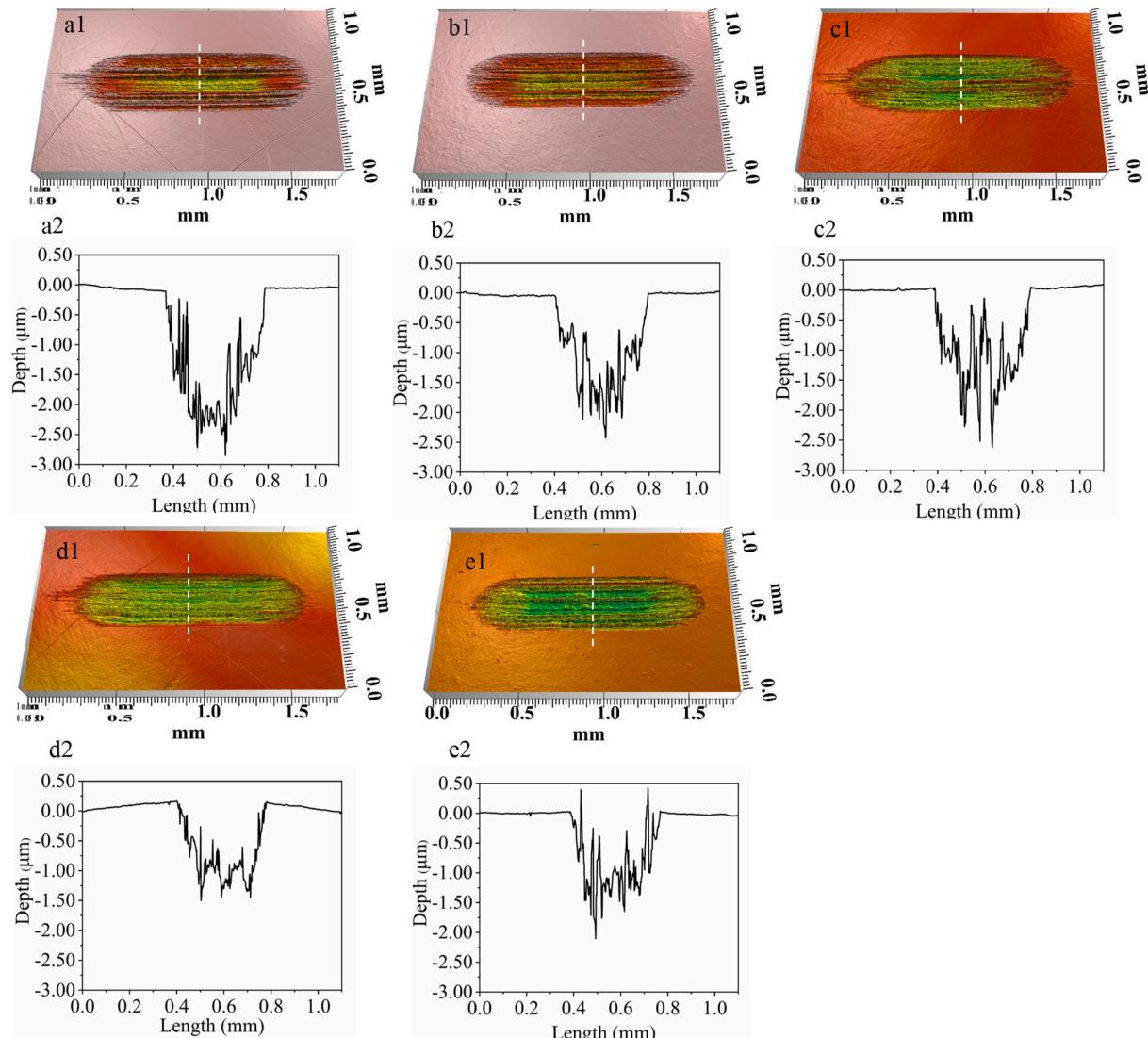


Fig. 6. 3D surface morphologies and depths of wear scars in SRV test disks lubricated with different CuP concentrations; (a1, a2) Li, (b1, b2) Li-1 wt%, (c1, c2) Li-2 wt%, (d1, d2) Li-3 wt% and (e1, e2) Li-4 wt%.

increasingly less severe. Notably, the surface of the wear scar from the Li-3 wt% sample was smooth and had the shallowest furrows. This was consistent with the test results in Fig. 6.

Fig. 8 shows SEM images of the wear scars lubricated with Li-3 wt% at 75 °C, 100 °C and 125 °C. The wear scars become slightly larger as the temperature increases. The furrows on the surface of the wear scars are shallower and flatter at 75 °C and 100 °C. When the temperature reached 125 °C, deeper furrows and small pits were formed on the surface of the wear marks.

The mechanism through which CuP improved the tribological properties of the lithium grease was investigated. The elemental maps of the wear scars on the Li-3 wt%-lubricated SRV test discs were generated with EDS and are shown in Fig. 9. The S, Cu and N originating from CuP were uniformly distributed on the surface of the wear scar. This indicated that the CuP adsorbed on the surface of the friction pairs formed a lubricating film. Consequently, the tribological properties of the lithium grease were improved [26].

To explain the mechanism through which CuP improved the tribological properties of the lithium grease, the elements and chemical states on the surface of the wear scar were analyzed via XPS. Fig. 10 shows the high-resolution S 2p, Cu 2p, N 1s and Fe 2p XPS spectra of the wear scars on the SRV test disks. The high-resolution XPS spectra for the surface of

the wear scar confirmed that S, Cu and N originated from CuP. In the S 2p spectrum, three peaks appeared at binding energies of 168.7 eV, 162.8 eV and 161.7 eV. The peak at 168.7 eV was attributed to FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, and the peaks at 162.8 eV and 161.7 eV were attributed to adsorbed CuP and newly formed FeS, respectively [27]. The Cu 2p peaks appeared at binding energies of 952.7 eV and 932.5 eV, corresponding to adsorbed CuP and newly formed Cu oxides, respectively [28]. A peak at 399.8 eV appeared for N, which corresponded to the N in the pyridine ring of CuP and nitrogen oxides. The Fe 2p peaks appeared at binding energies of 724.8 eV and 711.4 eV, corresponding to Fe_3O_4 , Fe_2O_3 , FeO , FeOOH and FeS, respectively [29]. In addition, the characteristic peaks of Cu 2p, N 1s and Fe 2p were not significantly different at different test temperatures. Similarly, the peak intensities of S 2p at 162.8 eV and 161.7 eV were not significantly different among the test temperatures. The peak at 168.7 eV was slightly stronger at the test temperature of 125 °C compared to 75 °C and 100 °C. This suggested that more sulfate was generated at higher temperatures. These results showed that CuP was adsorbed on the surface of the abrasive scar, some of which reacted with the surface of the scar through a tribochemical reaction to form a lubricating protective film. This approach improved the tribological properties of the lithium grease.

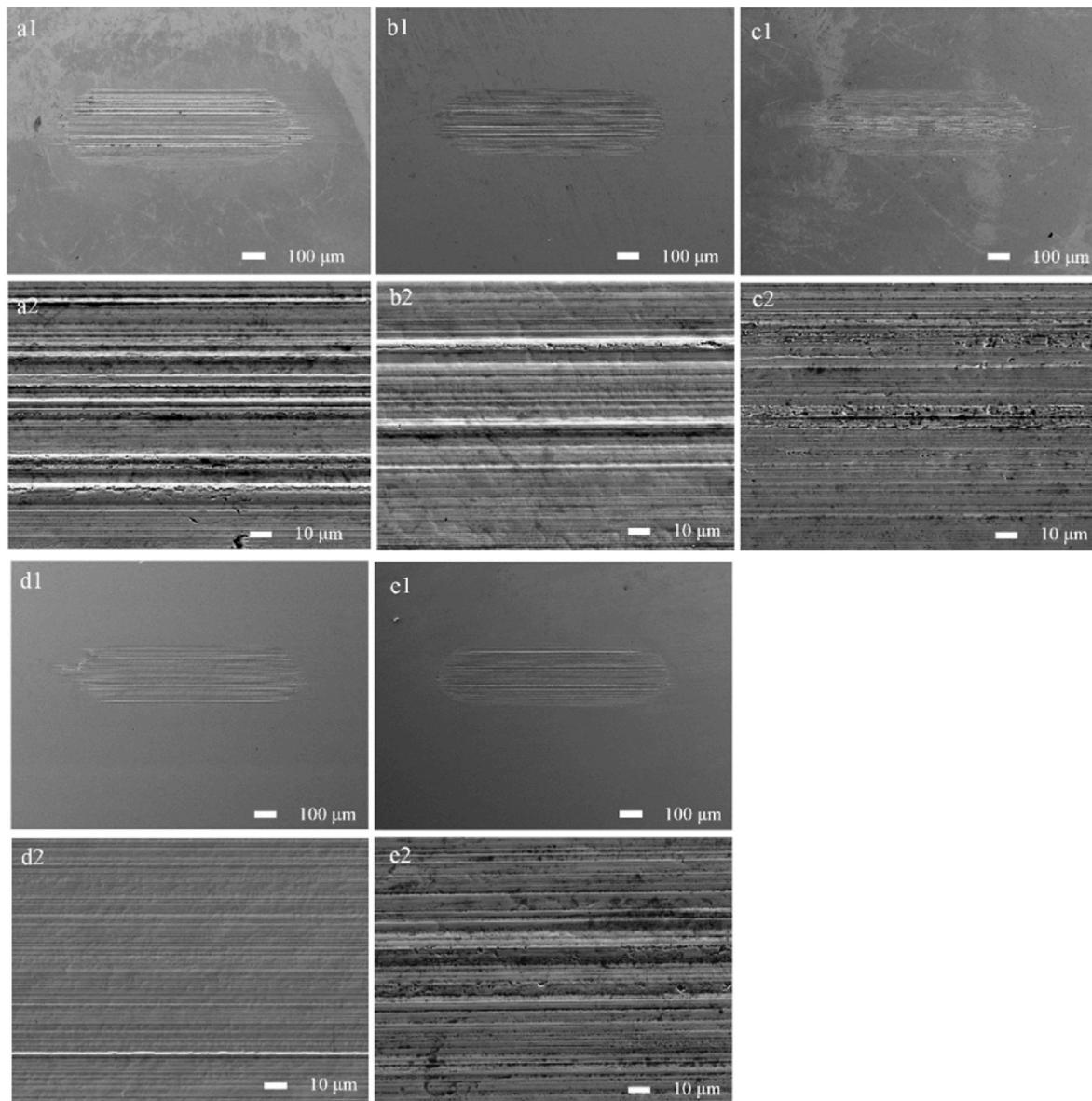


Fig. 7. SEM images of wear scars on SRV test disks lubricated with different CuP concentrations; (a1, a2) Li, (b1, b2) Li-1 wt%, (c1, c2) Li-2 wt%, (d1, d2) Li-3 wt% and (e1, e2) Li-4 wt%.

3.4. Antimicrobial properties

The antimicrobial performance test results are shown in Fig. 11. Bacterial growth on solid media coated by bacterial solutions with different concentrations revealed that the surfaces of the media with the blank sample and the sample Li were covered with bacterial colonies; in particular, especially the dilution times was 10^2 and 10^3 . Li demonstrated a negligible inhibitory effect on *S. aureus*. When the dilute times was 10^2 , there was only a small amount of colony growth on the surface of the medium with sample Li-3 wt%, and when the dilution times was 10^3 and 10^4 , there was no colony growth on the surface of the medium; that is, the antibacterial effect of Li-3 wt% on *S. aureus* was greater than 99.98%. The Li-3 wt% sample had a very good antibacterial effect on *S. aureus*. The addition of CuP resulted in excellent bacteriostatic performance for the Li-3 wt% sample.

3.5. Lubrication and antimicrobial mechanisms

Based on the test results, the lubrication mechanism and

antimicrobial mechanism of the CuP multifunctional additive used to improve the tribological properties and antimicrobial properties of lithium grease were explained.

A schematic diagram of the lubrication mechanism is shown in Fig. 12. CuP improved the friction reduction, antiwear and extreme pressure properties of the lithium grease. The primary reason for this was the presence of elements such as S, Cu, and N in the CuP. These elements formed a lubricating film on the wear surface via a combination of physical adsorption and tribochemical reaction [30]. At the beginning of the relative motion of the friction partner, CuP was adsorbed onto the surface of the friction pairs to form a physical adsorption film. Subsequently, in response to shear stress and frictional heat, the S, Cu and N and the friction pair surface of Fe and O underwent tribochemical reaction to generate iron oxides, iron sulfates, copper oxides and nitrogen oxides and form a chemical film. The physical adsorption and tribochemical reaction films together formed a lubricating film [31,32]. This prevented direct contact between the friction pairs, thereby reducing friction and wear. Additionally, it improved the extreme pressure performance. However, the sulfates generated from S

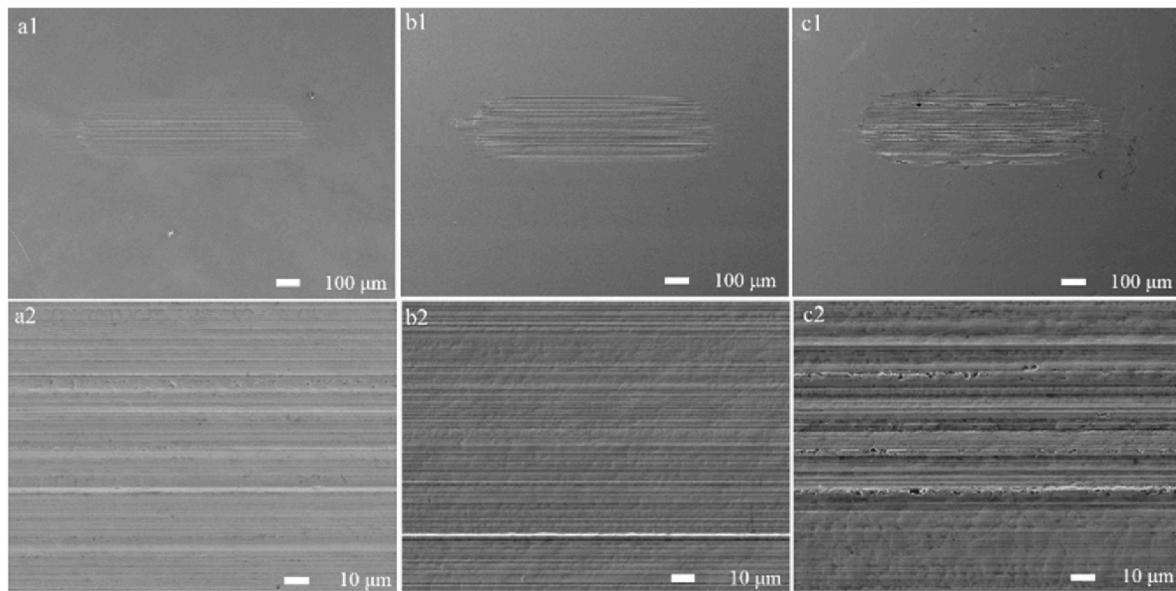


Fig. 8. SEM images of wear scars on SRV test disks lubricated with Li-3 wt% at 75 °C (a1, a2), 100 °C (b1, b2) and 125 °C (c1, c2).

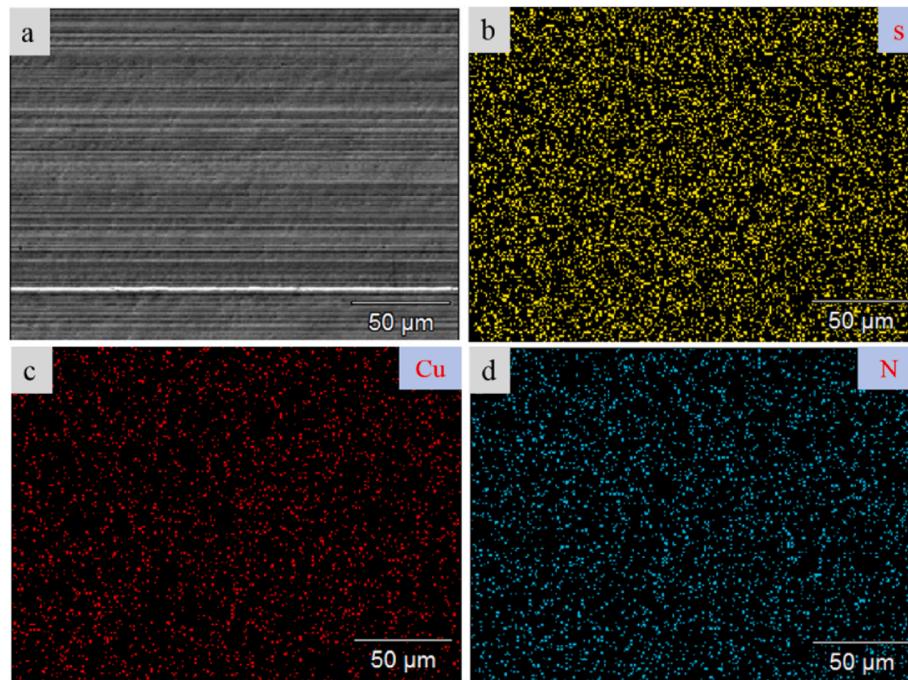


Fig. 9. SEM images and EDS analyses of the worn surface on an SRV test disk lubricated with Li-3 wt% at 100 °C.

were slightly corrosive to the surface of the friction pair, and when higher levels of CuP were added to the grease (4 wt%), more sulfates were generated by the tribochemical reaction, and the abrasive effect on the surface of the friction pair was enhanced [33]. As a result, more furrows and small pits were generated on the friction subsurface of the Li-4 wt% sample (see Fig. 7 e2) than on the wear scar surface of the Li-3 wt% sample. The coefficient of friction and wear volume of Li-4 wt% were slightly higher. Moreover, temperature significantly influences the tribochemical reaction. At a lower temperature of 75 °C, the reaction is slower and the formation of the lubrication film is insufficient. Consequently, the friction reduction and antiwear performance of CuP are slightly weaker. Conversely, at a higher temperature of 125 °C, the reaction is faster, leading to an increased generation of sulfate and an abrasive effect. This results in weaker friction reduction and antiwear

performance. However, at a temperature of 100 °C, a sufficient lubrication film is formed, thereby exhibiting optimal friction reduction and anti-wear performance [33,34].

Copper is integral to cellular physiology, but its excess can be detrimental as it catalyzes side electron transfer reactions, leading to the production of reactive oxygen species and oxidative damage to DNA, proteins, and lipids [35]. An excess of copper can also bind to proteins and biomolecules, and inhibit their functions. Consequently, an overabundance of copper ions disrupts bacterial cell growth, exerting an antibacterial effect. Moreover, pyridine heterocyclic compounds exhibit superior biological activities, characterized by high efficiency and low toxicity. Pyritthione, serving as an ionic carrier, interacts non-specifically with the plasma membrane and facilitates the transfer of copper ions to cells. This interaction enhances the activity of copper ions, thereby

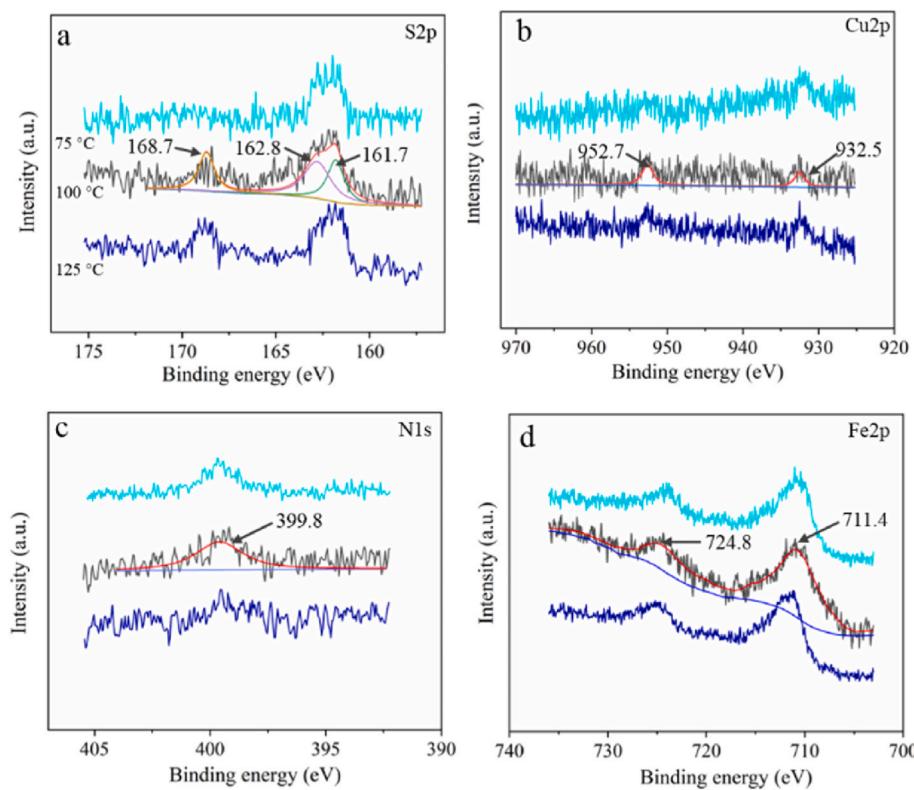


Fig. 10. S 2p, Cu 2p, N 1s and Fe 2p XPS spectra of the worn surface of an SRV test disk lubricated with Li-3 wt% at 75 °C, 100 °C and 125 °C.

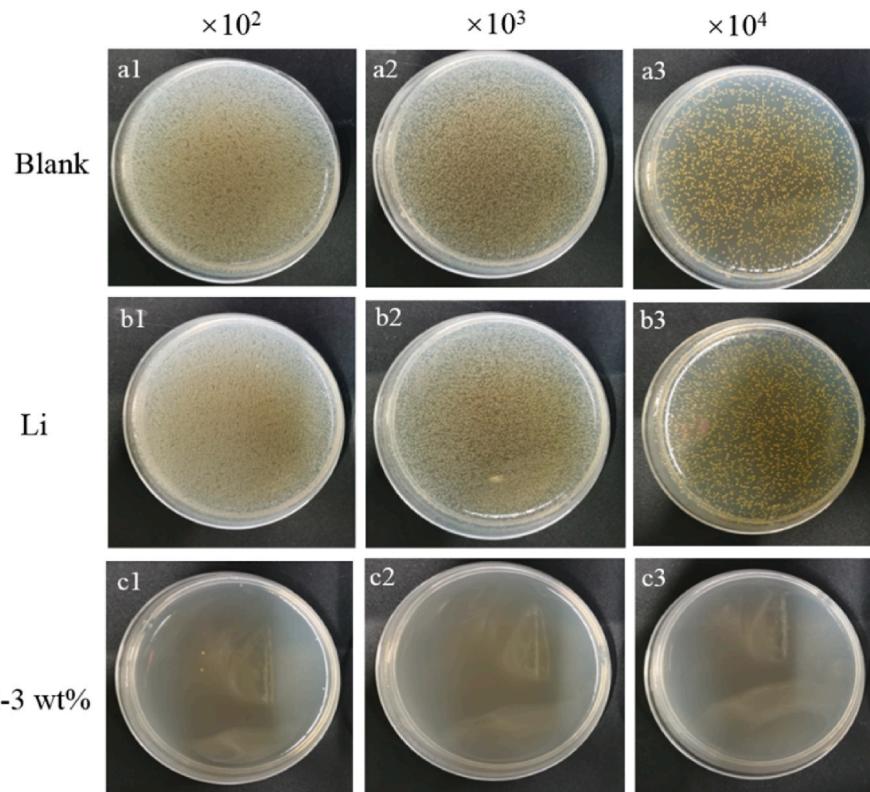


Fig. 11. Antimicrobial performance test. (a1, a2, a3) Blank sample, (b1, b2, b3) Li and (c1, c2, c3) Li-3 wt%.

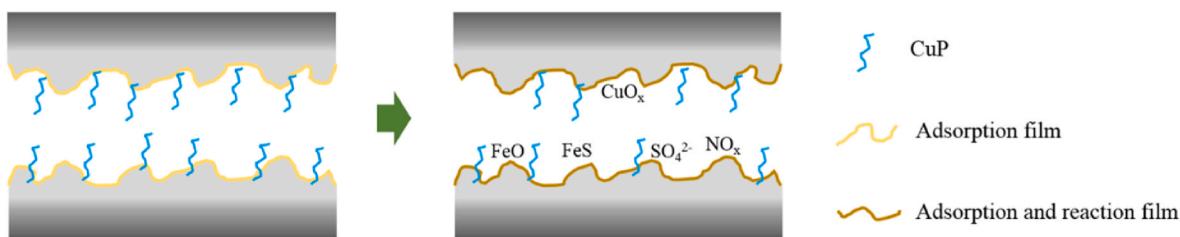


Fig. 12. Schematic diagram showing the lubrication mechanism.

augmenting the antibacterial efficacy of copper pyrithione [36,37]. This prevented deterioration of the lithium grease by bacteria and prolonged the storage and service life of the lithium grease.

4. Conclusions

CuP is used for the first time as a multifunctional additive in lithium grease. CuP not only enhances the friction reduction, antiwear and extreme pressure properties of lithium grease, but also gives it significant antimicrobial properties. The experimental results and mechanism are as follows.

- (1) The tribological performance results revealed that the addition of CuP significantly enhanced the friction reduction, antiwear properties, and extreme pressure properties of lithium grease. The results from the SRV tester indicated that CuP significantly improved the friction reduction and antiwear properties of lithium grease. The optimum addition amount in lithium grease was 3 wt%. The temperature at which the optimal friction reduction and antiwear performances were observed was 100 °C. Additionally, four-ball experimental results also demonstrated that CuP improved the friction reduction and antiwear properties of the lithium grease. Notably, the extreme pressure performance of the lithium grease containing 3 wt% CuP was improved by 3.17 times.
- (2) The incorporation of CuP significantly enhanced the antimicrobial performance of the lithium grease. Specifically, the bacterial inhibition rate of lithium grease with 3 wt% CuP was higher than 99.98%.
- (3) The formation of a lubrication film on the surface of the friction pairs by CuP, achieved through adsorption and tribochemical reaction, enhanced the lithium grease's performance in terms of friction reduction, wear resistance, and extreme pressure. Furthermore, the antimicrobial properties of the lithium grease were improved due to the detrimental and inhibitory impact of Cu²⁺ on cellular growth functions.

CRediT authorship contribution statement

Ren Jia: Writing – original draft, Methodology, Formal analysis. **Haopeng Cai:** Investigation, Data curation. **Gaiqing Zhao:** Writing – review & editing. **Zhuang Xu:** Writing – review & editing, Supervision, Conceptualization. **Xiaobo Wang:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- [1] H. Awad, K.M. Abdou, E. Saber, Steady state characteristics and stability limits of oil lubricated journal bearings using titanium dioxide nanoparticles as lubricant additives, *Results Eng* 20 (2023) 101486, <https://doi.org/10.1016/j.rineng.2023.101486>.
- [2] J. Zhang, A. Wheatley, R. Pasaribu, E. Worthington, S. Matthews, C. Zinser, et al., Wind turbine lubrication: low temperature fretting wear behaviour of four commercial greases, *Tribol. Int.* 187 (2023) 108706, <https://doi.org/10.1016/j.triboint.2023.108706>.
- [3] D.C. Benjumea, H. Laniado, O. Combita, Analytical model to monitor the oilconditions on the main components of mining dumpers, *Results Eng* 17 (2023) 100934, <https://doi.org/10.1016/j.rineng.2023.100934>.
- [4] L. Huo, J. Guo, F. Yang, C. Pan, H. Hu, K. Zhang, et al., Esterification of hydrogenated hydroxyl-terminated polybutadiene as a high-performance lubricating oil, *Ind. Eng. Chem. Res.* 61 (2022) 2685–2692, <https://doi.org/10.1021/acs.iecr.1c04314>.
- [5] B.M. Kamel, E.L. Arafa, A. Mohamed, Tribological and rheological properties of the lubricant containing hybrid graphene nanosheets (GNs)/titanium dioxide (TiO₂) nanoparticles as an additive on calcium grease, *J. Dispersion Sci. Technol.* 44 (2023) 2675–2682, <https://doi.org/10.1080/01932691.2022.2122491>.
- [6] B.M. Kamel, M. Naeem Awad, A. Mobasher, W. Hoziefa, Lithium–Calciumgreases having carbon nanotubes and aluminum oxide base nanoadditives: preparation and characteristics of nanogrease, *ACS Omega* 8 (2023) 38933–38940, <https://doi.org/10.1021/acsomega.3c03147>.
- [7] S.H. Musavi, M. Razfar, D.D. Ganji, New application of ionic liquid as a green-efficient lubricant, *Results Eng* 21 (2024) 101773, <https://doi.org/10.1016/j.rineng.2024.101773>.
- [8] L.R. Rudnick, *Lubricant Additives: Chemistry and Applications*, second ed., CRC, Boca Raton, 2009.
- [9] K. Zou, X. Lang, X. Liu, Q. Chen, P. Guo, Y. Liang, et al., Poly (ionic liquid)s with amino acids counterions as multifunctional water-based additives contributing to green lubrication, *Tribol. Int.* 192 (2024) 109295, <https://doi.org/10.1016/j.triboint.2024.109295>.
- [10] W. Li, Y. Wu, X. Wang, W. Liu, A study of P-N compound as multifunctional lubricant additive, *Lubr. Sci.* 23 (2011) 363–373, <https://doi.org/10.1002/lsc.162>.
- [11] K. Dey, G. Karmakar, M. Upadhyay, P. Ghosh, Polyacrylate-magnete nanocomposite as a potential multifunctional additive for lube oil, *Sci. Rep.* 10 (2020) 19151, <https://doi.org/10.1038/s41598-020-76246-4>.
- [12] R. Ma, Q. Zhao, E. Zhang, D. Zheng, W. Li, X. Wang, Synthesis and evaluation of oil-soluble ionic liquids as multifunctional lubricant additives, *Tribol. Int.* 151 (2020) 106446, <https://doi.org/10.1016/j.triboint.2020.106446>.
- [13] M. Cai, Y. Liang, F. Zhou, W. Liu, Tribological properties of novel imidazolium ionic liquids bearing benzotriazole group as the antiwear/anticorrosion additive in poly(ethylene glycol) and polyurea grease for steel/steel contacts, *ACS Appl. Mater. Interfaces* 3 (2011) 4580–4592, <https://doi.org/10.1021/am200826b>.
- [14] J. Wang, S. Ren, Z. Li, C. Wang, X. Huang, C. Fu, et al., Tribological behavior of a novel organic molybdenum containing mercaptotriazine as a multifunctional environmentally friendly additive, *Tribol. Int.* 159 (2021) 106988, <https://doi.org/10.1016/j.triboint.2021.106988>.
- [15] K.A. Karpov, A.V. Zachinyaeva, E.S. Geryainov, R.O. Olekhnovich, I.A. Ignateva, Investigation of biocidal properties of the lubricant additive mkf-18nt, *Pet. Chem.* 59 (2019) 1043–1048, <https://doi.org/10.1134/S0965544119090093>.
- [16] I.A. Aliev, L.A. Belovezhets, L.A. Oparina, Fungicidal activity of S-esters of thiocarboxylic acids as antimicrobial additives to petroleum products, *Pet. Chem.* 59 (2019) 99–105, <https://doi.org/10.1134/S096554411901002X>.
- [17] M. Rodríguez Ripoll, A.M. Tomala, L. Pirker, M. Remškar, In-situ formation of Mo₂ and WS₂ tribofilms by the synergy between transition metal oxide nanoparticles and sulphur-containing oil additives, *Tribol. Lett.* 68 (2020) 41, <https://doi.org/10.1007/s11249-020-1286-0>.
- [18] M. Zhu, N. Song, S. Zhang, Y. Zhang, L. Yu, G. Yang, et al., Effect of micro nanostructured copper additives with different morphology on tribological properties and conductivity of lithium grease, *Tribol. Trans.* 65 (2022) 686–694, <https://doi.org/10.1080/10402004.2022.2074589>.

- [19] C. Bressy, J.F. Briand, S. Lafond, R. Davy, F. Mazeas, B. Tanguy, et al., What governs marine fouling assemblages on chemically-active antifouling coatings? *Prog. Org. Coat.* 164 (2022) 106701 <https://doi.org/10.1016/j.porgcoat.2021.106701>.
- [20] R. Ciriminna, F.V. Bright, M. Pagliaro, Ecofriendly antifouling marine coatings, *ACS Sustainable Chem. Eng.* 3 (2015) 559–565, <https://doi.org/10.1021/sc500845n>.
- [21] V.D. Dasireddy, J. Kladnik, R.C. Korošec, B. Likozar, I. Turel, Pyrithione metal (Cu, Ni, Ru) complexes as photo-catalysts for styrene oxide production, *Sci. Rep.* 11 (2021) 23810, <https://doi.org/10.1038/s41598-021-03085-2>.
- [22] Z. Li, S. Wang, X. Yang, H. Liu, Y. Shan, X. Xu, et al., Antimicrobial and antifouling coating constructed using rosin acid-based quaternary ammonium salt and N-vinylpyrrolidone via RAFT polymerization, *Appl. Surf. Sci.* 530 (2020) 147193, <https://doi.org/10.1016/j.apsusc.2020.147193>.
- [23] J. Hong, B.S. Kim, B. Hou, S. Pak, T. Kim, A.R. Jang, et al., Room temperature wafer-scale synthesis of highly transparent, conductive CuS nanosheet films via a simple sulfur adsorption-corrosion method, *ACS Appl. Mater. Interfaces* 13 (2021) 4244–4252, <https://doi.org/10.1021/acsami.0c21957>.
- [24] S. Das, J.A. Robinson, M. Dubey, H. Terrones, M. Terrones, Beyond graphene: progress in novel two-dimensional materials and van der Waals solids, *Annu. Rev. Mater. Res.* 45 (2015) 1–27, <https://doi.org/10.1146/annurev-matsci-070214-021034>.
- [25] C. Wang, Y. Guo, Y. Yang, S. Chu, C. Zhou, Y. Wang, et al., Sulfur-doped polyimide photocatalyst with enhanced photocatalytic activity under visible light irradiation, *ACS Appl. Mater. Interfaces* 6 (2014) 4321–4328, <https://doi.org/10.1021/am500007u>.
- [26] C. Zang, M. Yang, E. Liu, Q. Qian, J. Zhao, J. Zhen, et al., Synthesis, characterization and tribological behaviors of hexagonal boron nitride/copper nanocomposites as lubricant additives, *Tribol. Int.* 165 (2022) 107312, <https://doi.org/10.1016/j.triboint.2021.107312>.
- [27] X. Wei, W. Li, X. Fan, M. Zhu, MoS₂-functionalized attapulgite hybrid toward high-performance thickener of lubricating grease, *Tribol. Int.* 179 (2023) 108135, <https://doi.org/10.1016/j.triboint.2022.108135>.
- [28] X. Jia, J. Huang, Y. Li, J. Yang, H. Song, Monodisperse Cu nanoparticles @ MoS₂ nanosheets as a lubricant additive for improved tribological properties, *Appl. Surf. Sci.* 494 (2019) 430–439, <https://doi.org/10.1016/j.apsusc.2019.07.194>.
- [29] Z. Wang, R. Ren, H. Song, X. Jia, Improved tribological properties of the synthesized copper/carbon nanotube nanocomposites for rapeseed oil-based additives, *Appl. Surf. Sci.* 428 (2018) 630–639, <https://doi.org/10.1016/j.apsusc.2017.09.207>.
- [30] Q. Lu, T. Zhang, Y. Wang, S. Liu, Q. Ye, F. Zhou, Boron–nitrogen codoped carbon nanosheets as oil-based lubricant additives for antioxidation, antiewear, and friction reduction, *ACS Sustainable Chem. Eng.* 11 (2023) 11867–11877, <https://doi.org/10.1021/acssuschemeng.3c01633>.
- [31] C. Zhang, Z. Lu, F. Li, L. Jia, Z. Yang, G. Chen, et al., Corrosion and lubrication properties of a halogen-free Gemini room-temperature ionic liquid for titanium alloys, *Tribol. Int.* 156 (2021) 106850, <https://doi.org/10.1016/j.triboint.2020.106850>.
- [32] C.L. Ong, Y.C. Lai, T. Heidelberg, W.K. Tang, V.S. Lee, N.G. Khaligh, et al., Highly effective ashless and non-corrosive dimercaptobenzothiadiazole as multifunctional lubricant additives in naphthenic base oil, *RSC Adv.* 13 (2023) 30733–30742, <https://doi.org/10.1039/D3RA05692A>.
- [33] K. Sangita, G. Rashmi, K. Aruna, K. Niranjan, S. Hiroyuki, Alkyl-chain-grafted hexagonal boron nitride nanoplatelets as oil-dispersible additives for friction and wear reduction, *ACS Appl. Mater. Interfaces* 7 (2015) 3708–3716, <https://doi.org/10.1021/am5083232>.
- [34] B. Chen, L. Liu, C. Zhang, S. Zhang, Y. Zhang, P. Zhang, Tribological properties and lubrication mechanism of protic ionic liquid-modified nanosilica as high-temperature antiwear additive for pentaerythritol ester, *Tribol. Int.* 176 (2022) 107886, <https://doi.org/10.1016/j.triboint.2022.107886>.
- [35] N. Husain, R. Mahmood, Copper (II) generates ROS and RNS, impairs antioxidant system and damages membrane and DNA in human blood cells, *Environ. Sci. Pollut. Res.* 26 (2019) 20654–20668, <https://doi.org/10.1007/s11356-019-05345-1>.
- [36] A. Mishra, K.Y. Djoko, Y.H. Lee, R.M. Lord, G. Kaul, A. Akhir, et al., Water-soluble copper pyrithione complexes with cytotoxic and antibacterial activity, *Org. Biomol. Chem.* 21 (2023) 2539–2544, <https://doi.org/10.1039/D2OB01224C>.
- [37] J.M. Zaengle-Barone, A.C. Jackson, D.M. Besse, B. Becken, M. Arshad, P.C. Seed, et al., Copper influences the antibacterial outcomes of a β-Lactamase-activated prochelator against drug-resistant bacteria, *ACS Infect. Dis.* 4 (2018) 1019–1029, <https://doi.org/10.1021/acsinfecdis.8b00037>.