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Tribological properties and lubricating mechanisms of Cu nanoparticles in lubricant

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Abstract: Wear and friction properties of surface modified Cu nanoparticles as 50CC oil additive were studied. The effect of temperature on tribological properties of Cu nanoparticles was investigated on a four-ball tester. The morphologies, typical element distribution and chemical states of the worn surfaces were characterized by SEM, EDS and XPS, respectively. In order to further investigate the tribological mechanism of Cu nanoparticles, a nano-indentation tester was utilized to measure the micro mechanical properties of the worn surface. The results indicate that the higher the oil temperature applied, the better the tribological properties of Cu nanoparticles are. It can be inferred that a thin copper protective film with lower elastic modulus and hardness is formed on the worn surface, which results in the good tribological performances of Cu nanoparticles, especially when the oil temperature is higher.

Key words: Cu nanoparticles; tribological property; lubricating mechanism; protective film; temperature

1 Introduction

Numerous studies have been carried out in recent years on the effects of various inorganic nanoparticles as lubricating oil additives on wear and friction[1−4]. Due to the remarkable tribological properties of nanoparticles, together with their good self-repair function to the worn surface, and good environmental-friendly property (without or with a little S, P and Cl), they have been desired for an excellent candidate for traditional lubricant additives, especially at severe frictional conditions, such as high temperature, high load and high sliding speed[5−7]. Among those that were added into oils, Cu (including Cu alloy) nanoparticles have received much attention and exhibited excellent applications for their good friction reduction and wear resistance properties [8−11]. Many influencing factors have been considered and the tribological behaviors of Cu nanoparticles as additive have been investigated, such as the concentration of nanoparticles in oil, sliding speed, applied load, contact form of friction pairs and lubricating oils[12].

However, few researchers have studied the high temperature tribological behaviors of Cu nanoparticles. It is well-known that the actual service temperature of lubricating oil is very high (90−100 ℃ or even higher than 150 ℃). Therefore, it is very important to study the influence of temperature on the lubricating properties of Cu nanoparticles as additive.

Furthermore, although considerable efforts have been made to understand how nanoparticles work as additives in oil to reduce friction and wear, their mechanism is still not very clear and the uncertainties exist between the following two viewpoints: ball bearing mechanism[13−14] and film forming mechanism[15]. For the ball bearing mechanism, chemical/mechanical reactions do not occur, and the researchers consider it still as an assumption without direct experimental evidence due to the deficiency of in situ characterization method. For the later, our recent studies[16] indicate that local overheating in friction may initate deposition of copper and forming of a thin protective film on the worn surface, hence, the friction and wear have been reduced. However, few researchers have described the mechanical properties of the protective film[17]. It is clear that the

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mechanical properties of materials strongly influence the tribological behaviors, especially for coatings and thin solid films on a metal substrate. Hence, measuring the micro mechanical properties (nano hardness and elastic modulus) of the protective film that is formed by Cu nanoparticles would be helpful to understanding the tribological mechanism of nanoparticle additives and providing reference data for their practical application as lubricating materials.

In this work, the authors investigated the influence of oil temperature on the tribological properties of Cu nanoparticles as lubricant additive, analyzed the rubbed surface and measured the elastic modulus and nano-hardness of the protective film that is formed on the worn surface using a nano-indentation tester.

2 Experimental

2.1 Tribological test

Surface modified Cu nanoparticles were prepared by chemical reduction method and surface modification technique[18]. To protect Cu nanoparticles against oxidation as well as to reduce agglomeration degree, a mixture of resin acceptor, methylbenzene and amine compound was mixed with the particles in a globe mill for 24 h to produce an organic coating layer. TEM image and corresponding electric diffraction(ED) pattern show that the particles have an average particle diameter of 20 nm with a FCC structure (Fig.1). The modified Cu nanoparticles can be dispersed well in some organic solvents, such as chloroform, benzene, methylbenzene and lubricating oil. The results confirm that the existence of the surface modification layer can effectively prevent the agglomeration of Cu nanoparticles and provide good oil-dispersion ability.

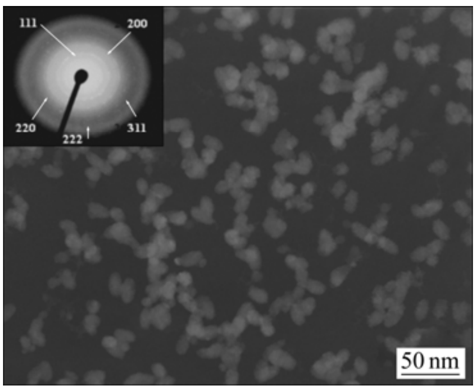

Fig.1 TEM image and ED pattern of Cu nanoparticles

Ball milling agitation and ultrasonic dispersion were used to provide good dispersion stability of Cu particles in 50CC oil. The effect of oil temperature on the tribological properties of Cu nanoparticles was studied on a four-ball tester. Its schematic diagram is shown in Fig.2. The balls used in the tests were made of SAE52100 steel with a diameter of 12.7 mm and a hardness of HRC 59−61. The tribological tests were carried out under the lubrication of 50CC pure oil and 50CC oil containing 0.2% (mass fraction) Cu nanoparticles. The oil was heated by a thermocouple and kept at a constant temperature. The experimental conditions were: atmospheric environment, rotation speed of 1 200 r/min, load of 294 N and test duration of 15 min. The oil temperatures were room temperature ((25±2) ℃, without heating), 50, 80, 110 and 140 ℃. For each sample, three identical tests were performed so as to minimize data scattering.

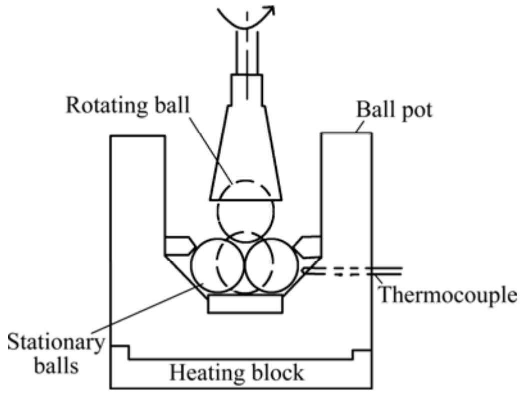

Fig.2 Schematic diagram of four-ball tester

2.2 XPS and nano-indentation analysis

XPS analyses were carried out to study the chemical state of the worn surface with PHI-5702 system using Mg K_{α} excitation ($h\nu$=1253.6 eV). The passing energy was 29.35 eV and the binding energy of C (1s) (284.6 eV) was used as a reference. The nano-indentation tests were performed using the indentation module of a Nano test 600 Micro Materials Nano Test System. A three sided pyramidal diamond indenter, with a diameter of 100 nm, was used throughout the tests. The initial load and the maximum load were 0.03 mN and 200 mN, respectively. The loading rate and unloading rate were both 0.3 mN/s and the holding duration (dwell time at the maximum load) was 5 s. For each sample, five points were measured and the average value was considered as the final hardness and elastic modulus of the sample.

3 Results and discussion

3.1 Tribological property and characterization

Fig.3 shows the effect of oil temperature on the friction coefficient and wear scar diameter for 50CC pure oil and 50CC oil containing Cu nanoparticles. It can be seen that the wear scar diameter(WSD) and friction coefficient of oil containing Cu nanoparticles are lower than those of pure oil. The friction and wear curves of pure oil rise rapidly with the increase of oil temperature, while the curves of oil containing Cu nanoparticles rise slowly and stably. By adding Cu nanoparticles into 50CC oil, the average wear scar diameter of the stationary balls at room temperature, 50℃, 80℃, 110℃ and 140 ℃ is reduced by 13%, 16%, 21%, 23% and 25%, respectively. And the friction coefficient is reduced by 5%, 8%, 10%, 15% and 20%, respectively. This indicates that the higher the temperature, the better the tribological properties of Cu nanoparticles are. Fig.4 shows the morphologies of the worn balls, indicating that wear grooves formed by wear particles are typical for the surfaces lubricated with 50CC pure oil, while the balls lubricated with oil containing Cu nanoparticles exhibit much smoother surfaces without severe scuffing.

Furthermore, the temperature sensor that is inserted in oil can measure and record the variation of the oil temperature during the tribological test (Fig.5). This shows that the temperature of 50CC oil containing Cu nanoparticles is lower. Moreover, the temperature curve is smooth and stable compared with that of 50CC pure oil. It is well known that when surfaces slide relatively, the energy dissipated in friction almost appears in the

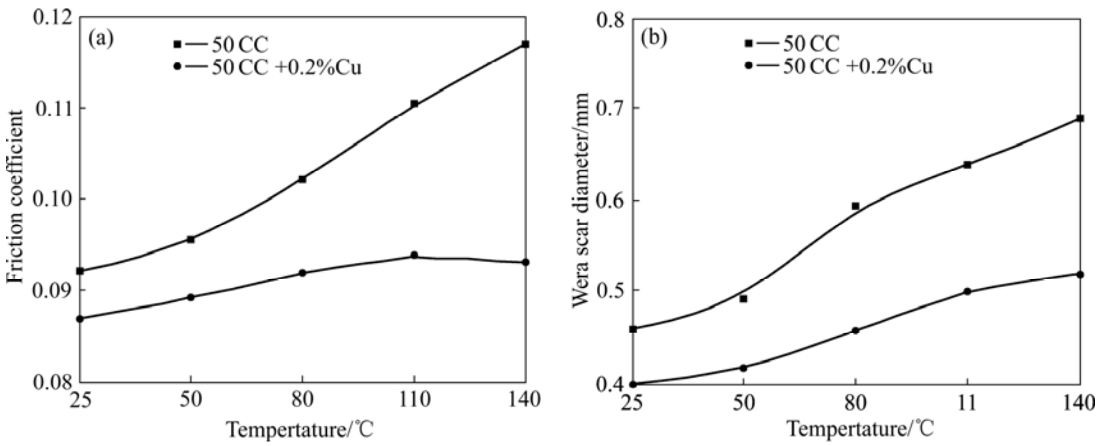

Fig.3 Tribological properties as function of temperature: (a) Friction coefficient; (b) Wear scar diameter

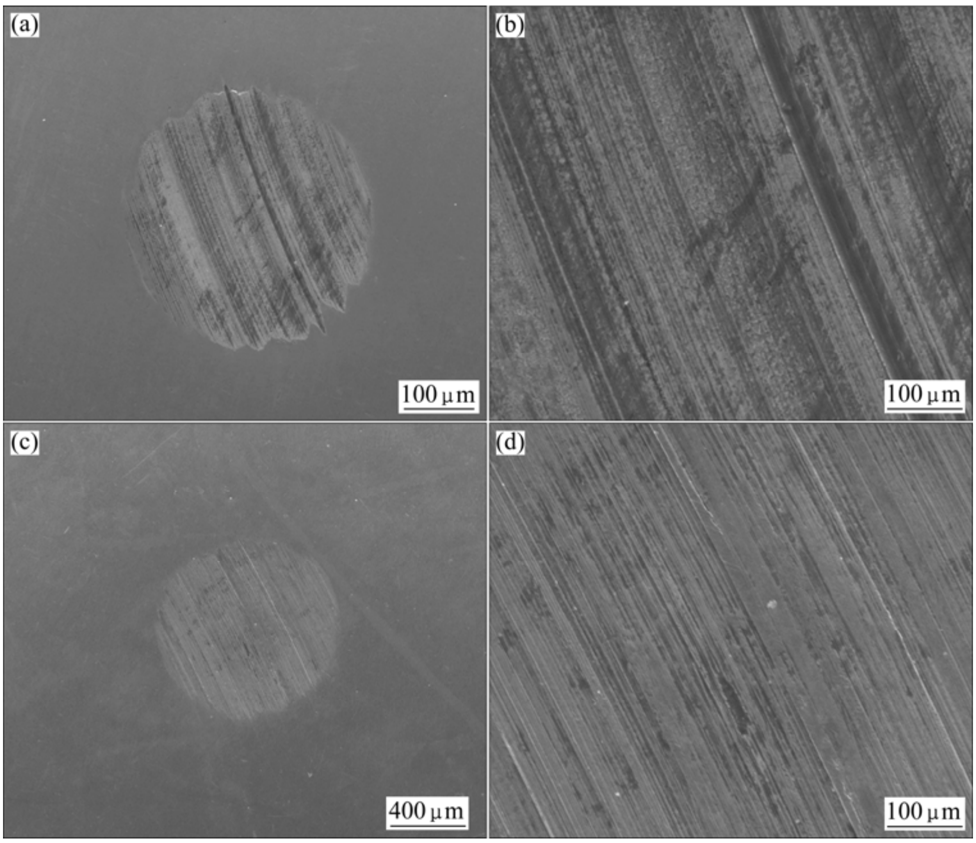

Fig.4 Typical SEM images of worn surfaces lubricated with different oil at 140 ℃: (a, b) 50CC; (c, d) 50CC+0.2%Cu

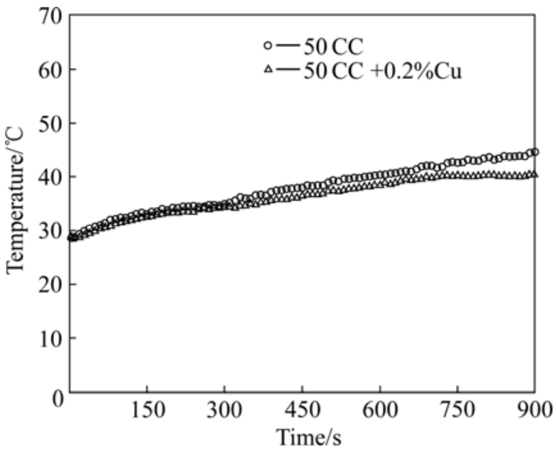

Fig.5 Variation of oil temperature for tests performed at room temperature

form of heat at the interface. This frictional heat raises the temperature of the interface and the oil. Fig.5 further indicates that Cu nanoparticles as additives have good friction reduction property.

3.2 Element analysis

Worn surfaces of the balls lubricated with oil containing Cu nanoparticles are found to be covered by a protective film. A uniform distribution of copper element is found along the friction direction by EDS (Fig.6). To further know the chemical states of the copper element, XPS analysis was conducted (Fig.7). It can be seen that the binding energy of Cu 2p is about 932.7 eV, responding to Cu^{+1} or Cu^0. Since Cu^{+1} is not stable[19], it can be inferred that the main substance of the film formed by Cu nanoparticles is simple substance of copper.

3.3 Micro mechanical properties

In order to study the micro mechanical properties of the copper film, nano-indentation tests were performed. Although the loading rate and initial and the maximum load are very low in the test, the effect of substrate on the mechanical properties of the thin copper film(with a thickness of 5 μm[20]) can not be ignored. Fig.8 shows the variation of indenter displacement with load. It is seen in Fig.8 that the depth of indenter on copper film is much larger than that of the worn surface lubricated with 50CC pure oil (50CC oil surface), indicating that the copper film formed on the worn surface is a soft thin layer and can deform easily.

In a nano-indentation test, the Micro Material System can automatically calculate the nano-hardness and reduced modulus, E_r, which is defined by[21]

$$1/E_r = (1-\nu_s^2)/E_s + (1-\nu_i^2)/E_i \quad (1)$$

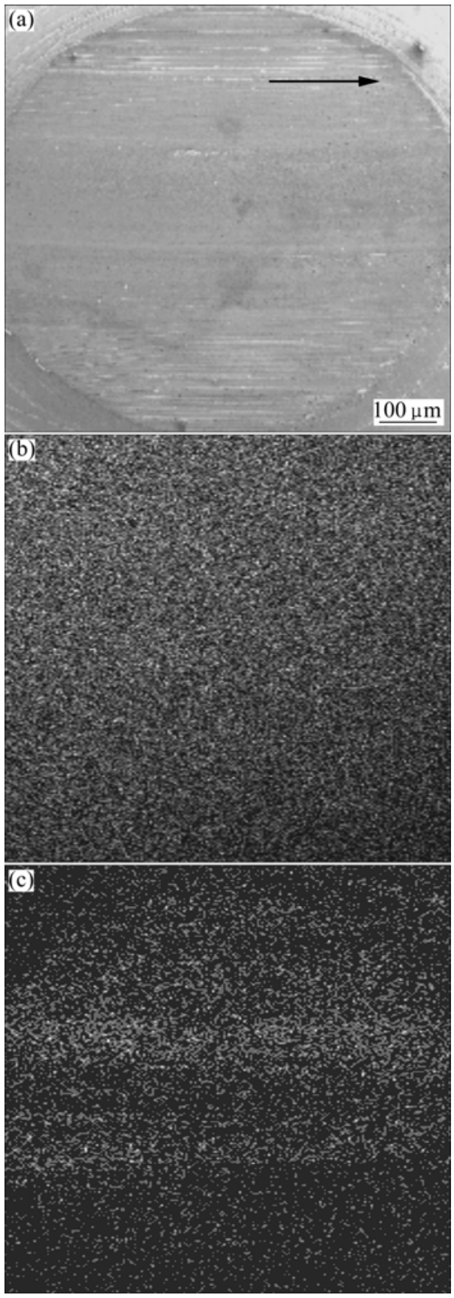

Fig.6 EDS analysis of worn surface lubricated with 50CC oil+0.2%Cu: (a) Surface morphology; (b) Fe distribution map; (c) Cu distribution map (Arrow indicates friction direction)

where ν_s is Poisson's ratio of the sample (0.28 for SAE52100 steel), ν_i is Poisson's ratio of the indenter(0.07), E_s is elastic modulus of the sample and E_i is elastic modulus of the indenter(1 141 GPa).

Therefore, the elastic modulus of the sample (worn surface), E_s, can be calculated and obtained. Table 1 gives the nano-hardness and the modulus of the worn surfaces. It can be seen that the nano-hardness and elastic modulus of the copper films are lower than those of 50CC oil surfaces. The micro mechanical properties of 50CC oil surfaces are stable without obvious change with the increase of temperature, while the nano-hardness

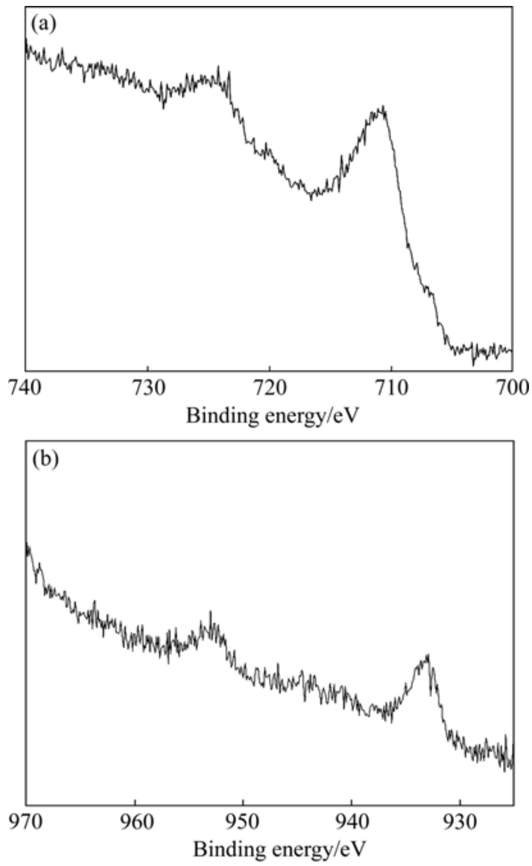

Fig.7 XPS analysis of worn surface lubricated with 50CC oil+0.2% Cu: (a) Fe 2p; (b) Cu 2p

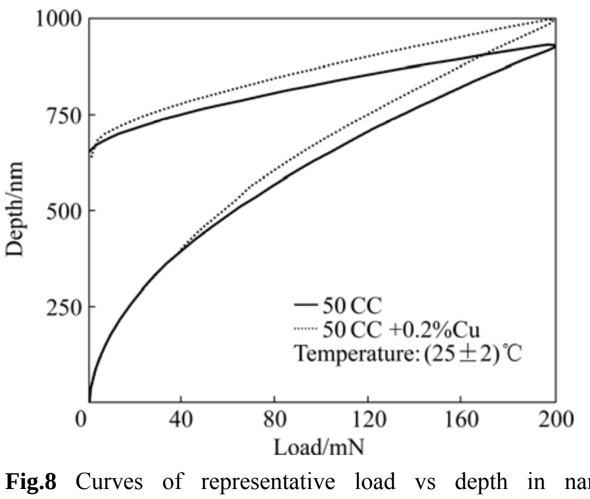

Fig.8 Curves of representative load vs depth in nano-indentation tests

and modulus of copper films decrease with increasing the oil temperature.

3.4 Tribological mechanism of Cu nanoparticles

In this study, a soft copper film with a low elastic modulus is found on the steel surface lubricated with 50CC oil containing Cu nanoparticles. The mechanism that how such a thin film is formed can be discussed on the basis of mechanical and metallurgy fundamentals. It is known that the flash temperature of friction surface is very high[22], while the melting point of Cu nanoparticles reduces from 1 073 ℃ to 490 ℃ compared with that of bulk materials[23]. Hence friction shearing force and high pressure at the interface can initiate the disengagement of Cu nanoparticles from their organic modified layers, and then high temperature due to direct contact of two surfaces originates melting of the bare Cu nanoparticles. In addition, due to good wetting property on steel surface, the liquid copper may well wet the friction pairs. Afterwards, it can be smeared on the worn surface by the shearing movement. Consequently, a copper protective film is formed.

By the reason that a thin soft film with low elastic modulus has been formed, three aspects of the tribological mechanism of Cu nanoparticles can be described.

Firstly, according to the tribological theory, the friction coefficient, f, can be expressed as[24]

$$f=S/P_0 \tag{2}$$

where P_0 is the yield strength of metals and S is the shearing stress on friction surface, representing the resistance to shear of the junctions and plastic flow of the weaker of the contacting materials.

If the influence of strain-hardening generated during the machining of the steel balls is ignored, the shearing stress on friction surface can be replaced by the shearing strength S_0 of metals, then we have

$$f=S_0/P_0 \tag{3}$$

Generally, the load-carrying ability of thin coating materials depends on the substrate, thus, in the case that a protective film has been formed on the worn surface (hard substrate), P_0 in Eqn.(3) is the yield strength of the

Table 1 Micro mechanical property of copper film and worn surface lubricated with 50CC oil

Temperature/℃	Nano-hardness/GPa		E_r/GPa		E_s/GPa	
	50CC oil	Copper film	50CC oil	Copper film	50CC oil	Copper film
25±2	13.08	12.15	190.20	160.827 6	210.15	172.40
50	12.94	11.74	185.90	146.424 3	204.47	154.72
80	13.15	11.58	193.45	140.360 6	214.40	147.40
110	13.01	11.55	184.62	149.141 5	202.80	158.41
140	13.3	11.4	186.30	140.861 8	205.17	148.21

steel ball. While the shearing action happens on the surface, the existence of a soft protective film can provide a lower shearing strength, S_0. As a result, the friction coefficient, f, is reduced.

Secondly, the results of the nano-indentation tests show that the copper film has a low elastic modulus compared with the worn surfaces lubricated with 50CC pure oil. That means, for a copper film, elastic deformation would occur more easily when a contact stress is applied in the same condition. In this case, wear particles would more easily pass the contact area between the friction surfaces and abrasive wear would be consequently reduced.

Finally, the existence of the soft film on the worn surface can increase contact area and provide fast relaxation and reduction of contact stress. Furthermore, the film separates two friction surfaces, avoids their direct contact and reduces adhesive wear.

As discussed above, the formation of a copper protective film with low hardness and elastic modulus on the worn surface can be considered as the main reason that oil containing Cu nanoparticles exhibits excellent lubricating properties. It is clear that the higher the temperature is, the more likely the melting of Cu nanoparticles and a soft film will be formed. Therefore, the friction and wear are reduced.

4 Conclusions

1) Cu nanoparticles as additives can effectively improve the lubricating properties of 50CC oil. Local high temperature and high pressure due to direct contact of two surfaces initiate melting of Cu nanoparticles and forming a copper protective film with low nano-hardness and elastic modulus on the worn surface.

2) The formation of copper film separates two friction surfaces and avoids their direct contacts. Furthermore, the low hardness of the film results in the reduction of friction, while the low elastic modulus increases the elastic deformation of the contact surface and reduces wear.

References

[1] XU Bin-shi. Nano surface engineering [M]. Beijing: Chemical Industry Press, 2004. (in Chinese)

[2] LIU Wei-min. Application of nanoparticles in lubricants [J]. Tribology, 2003, 23(4): 265−267. (in Chinese)

[3] SUN Lei, ZHOU Jing-fang, ZHANG Zhi-jun, DANG Hong-xin. Synthesis and tribological behavior of surface modified $(NH_4)_3PMo_{12}O_{40}$ nanoparticles [J]. Wear, 2004, 256: 176−181.

[4] RAPOPORT L, LESHCHINSKY V, LAPSKER I, VOLOVIK Y, NEPOMNYASHCHY O, LVOVSKY M, POPOVITZ-BIRO R, FELDMAN Y, TENNE R. Tribological properties of WS_2 nanoparticles under mixed lubrication [J]. Wear, 2003, 255: 785−793.

[5] XUE Qun-ji, LIU Wei-min, ZHANG Zhi-jun. Friction and wear properties of a surface-modified TiO_2 nanoparticle as an additive in liquid paraffin [J]. Wear, 1997, 213: 29−32.

[6] HU Z S, LAI R, LOU F, WANG L G, CHEN Z L, CHEN G X, DONG J X. Preparation and tribological properties of nanometer magnesium borate as lubricating oil additive [J]. Wear, 2002, 252: 370−374.

[7] QIU Sun-qing, DONG Jun-xiu, CHEN Guo-xu. Tribological properties of CeF_3 nanoparticles as additives in lubricating oils [J]. Wear, 1999, 230: 35−38.

[8] ZHOU Jing-fang, YANG Jian-jun, ZHANG Zhi-jun, LIU Wei-min, XUE Qun-ji. Study on the structure and tribological properties of surface-modified Cu nanoparticles [J]. Materials Research Bulletin, 1999, 34(9): 1361−1367.

[9] TARASOV S, KOLUBAEV A, BELYAEV S, LERNER M, TEPPER F. Study of friction reduction by nanocopper additives to motor oil [J]. Wear, 2002, 252: 63−69.

[10] FRISHBERG I V, KISHKOPAROV N V, ZOLOTUKHINA L V, KHARLAMOV V V, BATURINA O K, ZHIDOVINOVA S V. Effect of ultrafine powders in lubricants on performance of friction pairs [J]. Wear, 2003, 254: 645–651.

[11] ZHOU Jing-fang, ZHANG Zhi-jun, WANG Xiao-bo, LIU Wei-min, XUE Qun-ji. Investigation of the tribological behavior of oil-soluble Cu nanoparticles as additive in liquid paraffin [J]. Tribology, 2004, 20(2): 124−126. (in Chinese).

[12] QIAO Yu-lin. Lubrication and self-repair technology of nanoparticles [M]. Beijing: National Defense Industry Press, 2005. (in Chinese)

[13] YU Li-yan, HAO Chun-cheng, SUI Li-na, CUI Zuo-lin. Study on the improving friction and wear properties of lubricating oil with nanoparticles [J]. Journal of Material Science and Engineering, 2004, 22(6): 901−905. (in Chinese)

[14] QIAO Yu-lin, SUN Xiao-feng, XU Bin-shi, MA Shi-ning. High temperature tribological behaviors of nano-diamond as oil additive [J]. Journal of Central South University of Technology, 2005, 12(S2): 161−165.

[15] KHARLAMOV V V, ZOLOTUKHINA L V, FRISHBERG I V, KISHKOPAROV N V. The influence of Cu-Sn alloy fine powder on mass transfer subjected to sliding friction [J]. Friction and Wear, 1999, 20: 333−338.

[16] YU He-long, XU Bin-shi, XU Yi, WANG Xiao-li, LIU Qian. Design of wear-out-failure in-situ repair parts by environment-friendly nanocopper additive [J]. Journal of Central South University of Technology, 2005, 12(S2): 215−220.

[17] LIU Qian, XU Yi, SHI Pei-jing, YU He-long, XU Bin-shi. Analysis of self-repair films on friction surface lubricated with nano-Cu additive [J]. Journal of Central South University of Technology, 2005, 12(S2): 166−169.

[18] WANG Xiao-li, XU Bin-shi, XU Yi, YU He-long, SHI Pei-jing, LIU Qian. Preparation of nano-copper as lubricating oil additive [J]. Journal of Central South University of Technology, 2005, 12(S2): 203−206.

[19] MA Jian-qi, WANG Xiao-bo, FU Xing-guo, LIU Wei-min, CUI Ruo-mei. Investigation of the tribological properties of oil soluble Cu nanoparticles as additive in CD 15 W/40 diesel engine oil [J]. Tribology, 2004, 24(2): 134−138. (in Chinese)

[20] YU He-long. Preparation and tribological performance of surface modified Cu nanoparticles [D]. Beijing: Academy of Armored Force Engineering, 2006: 44−46.

[21] OLIVER W C, PHARR G M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments [J]. J Mater Res, 1992, 7(6): 1546−1583.

[22] BOWDON F P, TABOR D. The Friction and Lubrication of Solids [M]. Oxford: Clarendon Press, 1964.

[23] LIU Wei, DENG Xiao-yan, ZHANG Zhi-kun. Research of thermal stability of nano-copper particles [J]. PTCA (Part A: Physical Testing), 2004, 40(2): 64−67. (in Chinese)

[24] DONG Jun-xiu. Lubrication mechanism and lubricating oil [M]. Beijing: Hydrocarbon Processing Press, 1987. (in Chinese)

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