

## **Dispersion and their tribological properties of molybdenum nanoparticles with different particle sizes as additive in lubricating oil**

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Using silane coupling agent KH-570 as the surface modifier, molybdenum nanoparticles with various particle sizes were prepared by mechanical ball milling method. The molybdenum nanoparticles with different particle sizes were added into 900SN base oil to form the experimental lubricating oils. The dispersion of molybdenum nanoparticles in the lubricating oil was investigated by measuring the absorbance of the oil, and the tribological properties of the molybdenum nanoparticles as the lubricating oil additive were studied by a reciprocating friction tester. The results show that the molybdenum nanoparticles have good dispersion in the lubricating oil due to steric effect of the surface modified nanoparticles. The nanoparticles with smaller size exhibit better dispersion. Meanwhile, the excellent lubricating effect of the molybdenum nanoparticles in the lubricating oil is observed because these nanoparticles fill in some micro-pits on the worn surface. The particle size is smaller the better the repairing effect is for the worn surface. When the particle size of the molybdenum nanoparticles is about 40 nm, the molybdenum nanoparticles are dispersed well in the experimental lubricating oil and the oil shows good antifriction and antiwear performance.

**Keywords:** molybdenum nanoparticles, base oil, particle sizes, tribological property

Используя силановый связующий агент KH-570 в качестве модификатора поверхности, наночастицы молибдена с различными размерами частиц получали механическим методом шарового измельчения. Молекулярные наночастицы молибдена с различными размерами частиц добавляли в базовое масло 900SN для получения экспериментальных смазочных масел. Дисперсия наночастиц молибдена в смазочном масле изучалась путем измерения поглощения масла, а трибологические свойства наночастиц молибдена в качестве добавки к смазочным маслам изучались с помощью возвратно-ступательного фрикционного тестера. Результаты показывают, что наночастицы молибдена имеют хорошую дисперсию в смазочном масле из-за стерического эффекта поверхности-модифицированных наночастиц. Наночастицы с меньшим размером проявляют лучшую дисперсию. Наблюдается превосходное смазывающее действие наночастиц молибдена в смазочном масле, поскольку эти наночастицы заполняют некоторые микрешарики на изношенной поверхности. Чем меньше размер частиц, тем лучше восстанавливающий эффект для изношенной поверхности. Когда размер частиц наночастиц молибдена составляет около 40 нм, наночастицы молибдена хорошо диспергируются в смазочном масле, и масло приобретает хорошие антифрикционные и противоизносные свойства.

**Дисперсія і трибологічні властивості наночастинок молибдену з різними розмірами частинок в якості добавки у мастилі.** *Tianhua Chen*

Використовуючи силановий сполучний агент KH-570 в якості модифікатора поверхні, наночастинок молибдену з різними розмірами частинок отримували механічним методом кульового подрібнення. Молекулярні наночастинок молибдену з різними розмірами частинок додавали у базове масло 900SN для отримання експериментальних мастил. Дисперсія наночастинок молибдену в мастилі вивчалася шляхом вимірювання

поглинання олії, а трибологічні властивості наночастинок молибдену в якості добавки до мастил вивчалися за допомогою зворотно-поступального фрикційного тестера. Результати показують, що наночастинки молибдену мають хорошу дисперсію у мастилі завдяки стеричному ефекту поверхнево-модифікованих наночастинок. Наночастки з меншим розміром виявляють кращу дисперсію. Спостерігається чудове змащування дія наночастинок молибдену у мастилі, оскільки вони заповнюють деякі мікрочастиці на зношеній поверхні. Чим менше розмір часток, тим краще відновлюючий ефект для зношеної поверхні. Коли розмір часток наночастинок молибдену становить близько 40 нм, вони добре диспергують у мастилі, і масло набуває хороші антифрикційні та протизносні властивості.

## 1. Introduction

Nano materials as lubricant additives can significantly improve the anti-friction and anti-wear properties of lubricating oil [1]. With layered crystal structure, weak bonding force between layer and layer exist in the molybdenum metal. At the same time, under friction molybdenum is fragile, and prone to slip, which play an increasingly important part in anti-friction and repair [2]. Due to its high surface activity, when the particle size reaches nanometer scale, molybdenum is easy to generate "gobbet". It will not only down low as lubricating oil additive anti-friction and anti-wear effect, but also increase the wear degree of friction pair. In order to solve the agglomerate of nanoparticles in lubricating oil, the method of surface modification is often adopt to improve the dispersion stability of nanoparticles [3].

According to different properties of nanoparticles, different modifier modified should be adopted to make nanoparticles have electrostatic repulsion or space steric effect. Therefore, the degree of agglomerate phenomenon is reduced [4]. Improvement the dispersion of molybdenum nanoparticles that as lubricating oil additives is very significant for anti-friction resistance grinding effect in lubricating oil. In the paper, using silane coupling agent as surface modifier, the size of molybdenum nanoparticles on the dispersion of molybdenum nanoparticles in lubricating oil and the influence of friction performance were studied.

## 2. Experimental

Molybdenum nanoparticle were prepared by mechanical ball mill methods. 325 sieve mesh of molybdenum powder and GCr15 material were added into the ball mill grinding stainless steel tank at 70:1 ratio of ball; set the ball mill speed of 450 r/min. After that adding 1mL ethanol, wet milling for 3h, add 6mL anhydrous ethanol and 0.6 mL silane coupling agent KH-570 (surface modifier), the solutions is continue to ball mill. The process of ball mill run 30 min, 5 min

downtime, and different size of molybdenum nanoparticles were prepared. At last, ball grinding particles were prepared by washing, filtering and drying, get samples for test. Grinding ball valid time is 30, 35 and 40 h in the preparation of molybdenum nanoparticles, respectively, for sample 1 and sample 2 and sample 3.

The 0.5% molybdenum nanoparticles with different particle size were added to the 900 SN base oil, with a magnetic stirrer heating mixing at a speed of 1500 r/min, after 1 h and ultrasonic dispersion.

The lubricant oil of centrifugal experiments were used the TG16 - WS centrifuge table high speed centrifugal pipe. The absorbance of upper oil after a certain time centrifuge were measure. The test of centrifuge speed of 10000 r/min. The UV absorbance were measured by 5100 uv-vis spectrophotometer. The CFT is - type 1 material performance was used for reciprocating friction experiment, in order to investigate three different particle size of molybdenum friction properties of the nanoparticles under different friction conditions. The sample of the friction is GCr15 steel ball, the diameter of 4 mm, hardness of 60 ~ 66 HRC; sample of 45 steel steel plate, 24 mm diameter, high is 4 mm, hardness is 210 HB. Before the start of the test, steel ball, steel plate and the fixture were cleaned and dried with acetone ultrasonic cleaning. Friction conditions : load of 50 N, friction time for 30 min, friction velocity respectively 0.5 m/s, 0.075 m/s, and 0.1 m/s. Friction experiment repeated 3 times, the average value as the result of the experiment. Use with metallographic microscopes the worn surface morphologies were observed.

## 3. Results and discussion

### 3.1 Molybdenum nanoparticles dispersion

The variations of absorbance of the experimental lubricating oils with time are shown in the Fig. 1, when the mass fraction 5%, the nanoparticle size are 40, 65 and 85 nm. When the molybdenum nanoparticles are added to the 900 sn oil, because of

molybdenum nanoparticles of infrared light absorption and reflection infrared light, which make the IR light transmission performance variation in the lubricating oil result in increasing the absorption properties of lubricating oil. If the molybdenum nanoparticles in lubricating oil, the better dispersion, the red light will more chance to meet the nanoparticles on the transmission of light, the greater the absorbance of lubricating oil. Similarly, if the lubricating oil of molybdenum nanoparticles (that is, the more content), the more light absorption of lubricating oil is also enhanced. Fig.1 shows that grain size is smaller, the absorbance is greater under the same amount of molybdenum nanoparticles. The results indicated that small particle size of molybdenum nanoparticles have good phenomenon in lubricating oil dispersancy. In addition, with the increasing of centrifugal time, the absorbance of the sample are rendered as a downward trend.

Molybdenum mainly moves in Brownian motion when nano particles dispersed in lubricating oil. The molybdenum nanoparticles modified by silane coupling agent, the surface adsorb organic polymer layer, which make molybdenum nanoparticles has the space steric effect, enhanced touch each other, and form together due to Brownian motion. Therefore, Brownian movement makes molybdenum nanoparticles maintain a certain degree of dispersion in lubricating oil. When the lubricating oil for centrifugal trials, centrifugal force will produce certain directional movement, molybdenum pellet overcome Brownian motion, to from the bottom of the heart tube aggregation, as well as further increases the risk of molybdenum particle collision with each other together. Therefore, under the action of centrifugal force, large size of molybdenum particles experience deposition to the bottom of the centrifuge tube.

At the same time, the number of molybdenum nanoparticles decrease in lubricating oil, leading to lubricating oil absorbency decreases. Under the centrifugal force, the settlement of molybdenum nanoparticles in lubricating oil speed in the Stokes formula available:

$$v = \frac{r^2(\rho - \rho_0)\alpha\omega^2}{18\eta} \quad (1)$$

$r$  – stand for the diameter of the particles,  $\rho$  – the density of particles,  $\rho_0$  – the dispersing medium density,  $\alpha$  – the rotating

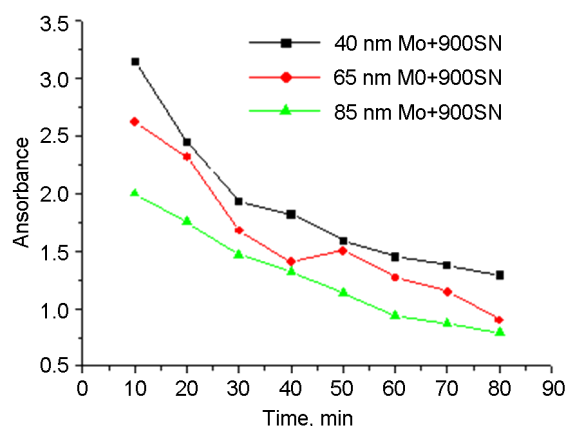


Fig.1. Variations of absorbance of the experimental lubricating oils with time

radius of particles,  $\omega$  – rotating angular velocity,  $\eta$  – dynamic viscosity of the dispersing medium. Equation (1) show that in the process of centrifugal, the settlement velocity of molybdenum nanoparticles is proportional to the square of the particle size, the particle size is smaller, settling velocity is slower. Therefore, settling velocity of 40 nm molybdenum nanoparticles than 65 nm and 85nm. The concentration of 40 nm molybdenum nanoparticles is biggest, so the measured absorbance value is higher than other size nanoparticles. The result indicate that under the same condition, the lubricating oil dispersion adding 40 nm nano diamond Grain is better than other lubricants.

### 3.2 Molybdenum friction and wear behavior of nanoparticles

As shown in Fig.2, with the increase friction velocity, friction factor of lubricating oil is obviously decreases, while the wear volume slowly increase. Under the same friction velocity, friction coefficient and volume wear quantity of lubricating oil containing molybdenum is smaller than of 900 SN base oil. Under different friction velocity, there are only different differences. Among them, friction factor and volume wear of 40 nm and 65 nm are very close. When the friction velocity is low (0.5 m/s, and 0.075 m/s), the friction factor of lubricating oil containing molybdenum 40 nm particles and volume wear quantity are smaller than 65 nm, 85 nm particles and 900 SN base oil. It shows that the tribological behavior of lubricating oil containing small size particles is better than that con-

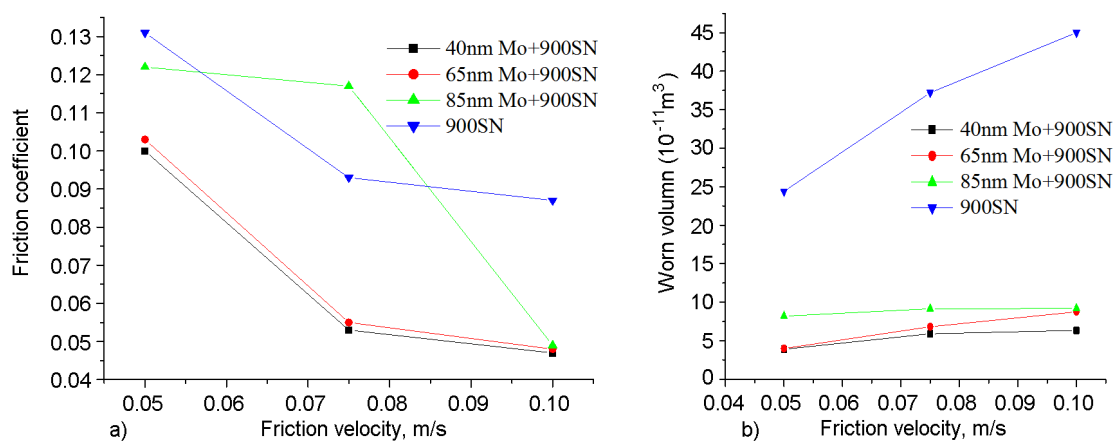


Fig.2. Variations of friction coefficient and worn volume of the experimental lubricating oils and 900 SN base oil with friction velocity ( a) friction coefficient; ( b) worn volume.



Fig.3. Micrographs of the worn surfaces of 45 steel lubricated with 900 SN base oil ( a) 0.05 m/s; ( b) 0.075 m/s; ( c) 0.1 m/s

taining the big size of molybdenum particles. When the friction velocity of 0.1 m/s, the friction factor of three kinds of molybdenum particle size particles lubricating oil are closer. Grinding ullage volume of lubricating oil containing 40 nm molybdenum particles is minimum. It can conclude that molybdenum nanoparticles can effectively improve the anti-wear performance of lubricating oil. The lubricating oil with smaller size molybdenum nanoparticles has good dispersion, the anti-friction and anti-wear effect more apparent.

### 3.3 Wear surface morphology

As shown in Fig.3, when the friction velocity is 0.5 m/s, 45 steel steel plate wear table surface appears only a small amount of grinding crack. With the increase of friction velocity, the wear volume increased significantly, grinding crack gradually change the width and the depth.

As shown in Fig.4, when the friction velocity is low (0.5 m/s, and 0.075 m/s), the surface of 45 # steel steel plate wear almost no grinding crack and wear surface is flat, when the friction speed is 0.1 m/s, the wear surface is slight grinding crack. When the friction velocity of 0.05 m/s, and 0.075 m/s,

the surface of 45 # steel plate wear there is a small amount of mild grinding crack, surface wear is small, and still keep the original processing traces as indicated in Fig.5. When the friction velocity is 0.1 m/s, wear surface grinding marks a slight widening and deepening. As shown in Fig.6, 85 nm particles as lubricating oil additives, when the friction velocities are 0.05 m/s, and 0.075 m/s, the surface of 45 # steel steel plate mill loss relatively flat. When the friction velocity is 0.1 m/s, the more obvious grinding crack form.

From Fig.3, Fig.4, Fig.5 and Fig.6, under the same conditions, it can be found that the degree of friction velocity of 900 sn base oil containing molybdenum nano diamond particles is change with the nanoparticles size. The number of steel plate surface grinding crack the width and depth of 45 steel are obviously lower.

The results shows that molybdenum nano particle size is smaller, the number of steel plate surface grinding crack of 45 steel, width and depth is less obviously, the wear surface is more smooth. With the increase of friction velocity, the steel plate of wear surface is damaged more serious.

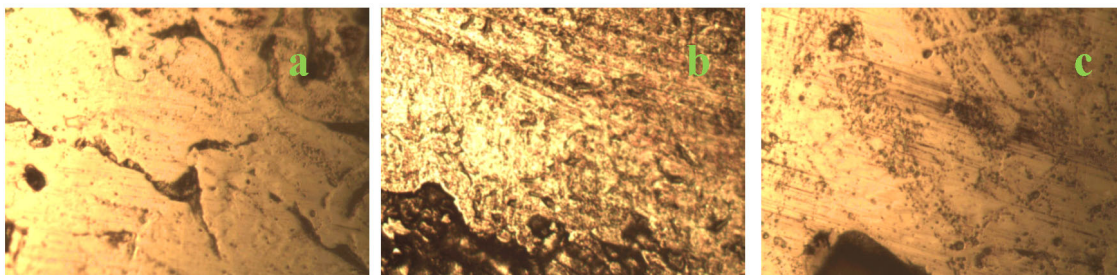


Fig. 4. Micrographs of the worn surfaces of 45 steel lubricated with 900 SN oil containing 40 nm antimony nanoparticles (a) 0.05 m/s; (b) 0.075 m/s; (c) 0.1 m/s.

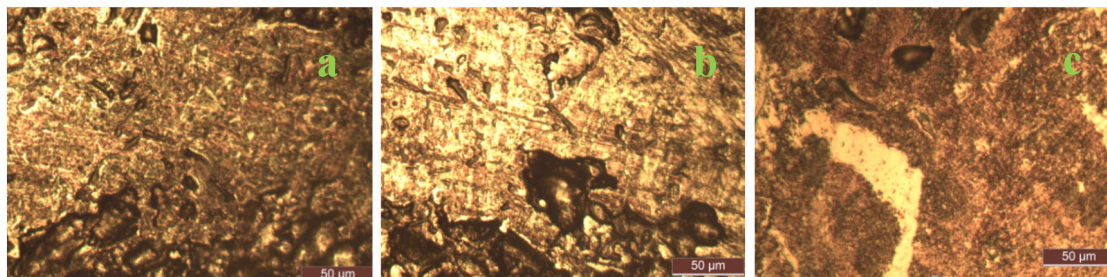


Fig. 5. Micrographs of the worn surfaces of 45 steel lubricated with 900 SN oil containing 65 nm antimony nanoparticles (a) 0.05 m/s; (b) 0.075 m/s; (c) 0.1 m/s.

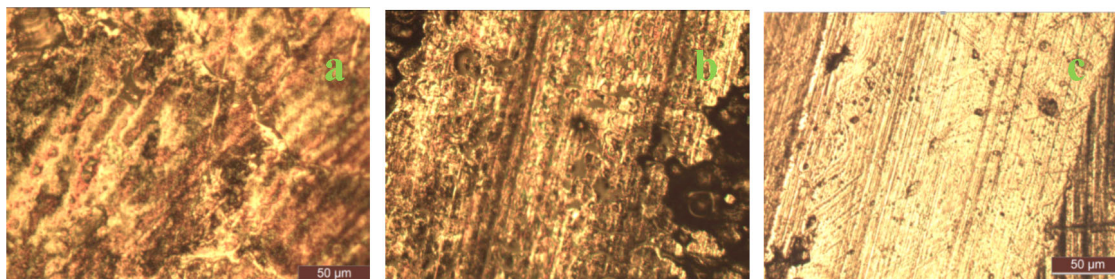


Fig. 6. Micrographs of the worn surfaces of 45 steel lubricated with 900 SN oil containing 85 nm antimony nanoparticles (a) 0.05 m/s; (b) 0.075 m/s; (c) 0.1 m/s.

#### 4. Conclusions

Silane coupling agent KH - 570 can be effectively adsorbed on the surface of molybdenum nanoparticles prepared by the mechanical ball mill method. Due to the existence of space steric effect, the molybdenum nanoparticles has better dispersion and stability.

When the 900 SN base oil containing different particle size of nanometer granule, under the action of centrifugal force, molybdenum nanoparticles can produce subsidence phenomenon. If molybdenum nanoparticles size is small, particles can be overcome in a definite degree of subsidence caused by centrifugal force due to Brownian motion. The particle size is smaller, the sink down phenomenon is lighter, the dispersion of particles in the lubricating oil is better.

For 900 SN base oil, molybdenum nanoparticles as additive can effectively improve the anti-friction and anti-wear effect

of lubricating oil. The particle size of nanometer particles is smaller, the effect of anti-friction and anti-wear are better.

When molybdenum nanoparticles size is 40 nm, the lubricating oil showed excellent antifriction grinding resistance.

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