Tribological performances of multilayer-MoS_2 nanoparticles in water-based lubricating fluid

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Abstract. Multilayer-MoS_2 nanoparticles were dispersed in water-based lubricating fluid in a convenient and economical way. Oleic acid and triethanolamine were used as the main surfactants in this solution. Tribological performances of this fluid were tested under high pressure and high rotating speed. FEI Tecnai G20 TEM, Malvern Zetasizer Nano ZS were used to study the particle size and Zeta potential of the lubricants. Tribological performances of this water system with multilayer-MoS_2 nanoparticles and the 3D-surfaces of wear scars after the experiments were analyzed by means of four-ball wear test machine and Olympus laser confocal microscope. According to Hertz theory and experimental data, it is practical significance to combine MoS_2 nanoparticles with water-based lubricating fluid. Under high loading and high rotating speed the mixed suspension can provide good lubricating properties. On the basis of calculation the binding energy of layers in MoS_2 nanoparticles is less than the energy of shearing in friction pairs. The layers in MoS_2 nanoparticles slide in the process of friction. The best lubrication effects can be displayed when friction process lasts about 500 s.

Keywords: Water-based lubricating fluid, Multilayer-MoS_2 nanoparticles, Four-ball tribological test

1. Introduction

With the improvement of nanotechnology and the much deeper research of nano-tribology, scholars all over the world have made a lot of researches on nanoparticles as a new type of lubricant additives [1-2]. Water-based lubricating fluid has become a hot research topic with the advantages of good cleaning property, energy saving, environmental friendly, large heat capacity and so on [3]. At present, it has been proved that the nanoparticles can bring in good lubrication and cooling effects [4]. Yaohua Xu used water-soluble nano-copper as an additive, which improved the performance of wear and friction reducing, and thus enhanced the thermal conductivity of the solution [5]. Liang et al. has confirmed that the ultrathin graphite sheet had a good lubrication effect as the additives of the water-based lubricant. MoS_2 is similar to the structure of graphite and widely used in the process of lubrication. The fracture strength of single-layer MoS_2 is 16 GPa-30 GPa, which has been determined by S Bertolazzi et al. Showing the single-layer MoS_2 have good mechanical properties [7]. When the solid MoS_2 reach the nanometer scale, the physicochemical properties are better than the ordinary solid MoS_2 [8-9]. Qingjuan Meng carried out the researches on water dispersible nanometer MoS_2 [10]. But there are still not enough researches on the tribological properties of MoS_2 nanoparticles as water-based lubricating fluid additives [11].

Currently, most of the researches on the nanoparticle lubrication mechanism are proceeded within low pressure and low rotating speed, which is far from the actual production processes [12-13]. Furthermore, the ultra-thin graphite, fullerene like MoS_2 and single-layer nano-MoS_2 as the research objects of water-based lubricant additives are higher production costs, less application in actual production, in that it is necessary to carry researches about the application and mechanism with the combination of multilayer-MoS_2 nanoparticles and water-based lubricant. Because of oleic acid and triethanolamine are lamellar liquid crystal structure, not affected by pH, low requirement of working environment [14], and the reactant of oleic acid triethanolamine ester under high temperature, which has good lubricity and corrosion resistance [15]. All of the three reagents are conducive to degradation and smaller affection of pollution. In this experiment, we use oleic acid / triethanolamine as a water-based lubricant system. So in this paper, multilayer-MoS_2 was dispersed in the acid / triethanolamine water system to study the tribological properties under high pressure and high rotating speed.

2. Experiment

2.1. Preparation of water-based lubricating fluid with nanoparticles

The use of sodium dodecyl benzene sulfonate (SDBS) as surfactant, sodium polyacrylate as stabilizer, aqueous boric acid esters as both extreme pressure agent and anti-rust agent, sodium hydrogen diacetate as preservatives, 2, 2, 4-Trimethyl-1, 3-pentanediol monoisobutyrate (cs-12) as film-forming agent disperse the nanoparticles in the nominal particle size 100 nm in water-based lubricant. Figure 1 is the flow chart for the preparation of the quality score of 0.1% water-based lubricant with nanoparticles:

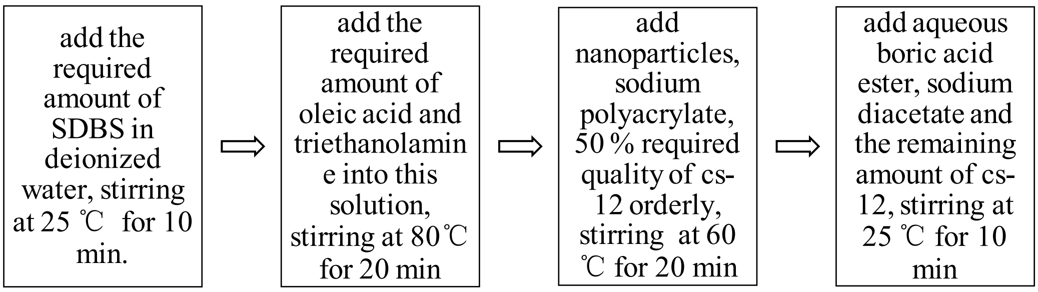

Figure 1. Flow chart of preparing water-based lubricating fluid with MoS_2 nanoparticles.

2.2. Tribological test

Based on the American standard ASTM D2783-2003, the tribological properties of the water-based nano-lubricant were tested by four-ball wear test machine, determination of the last non-seizure value (P_B) of the lubricant and the friction coefficient under different load. In the condition of 588 N load, the friction coefficient at different speeds was measured. Three-dimensional morphologies of the steel balls after long milling were analyzed by Olympus laser confocal microscope. Special steel balls were used for four ball testing machine. The steel ball material is GCr15A, the diameter is 12.7 mm, and the hardness is HRC 64 - 66.

3. Results and discussion

3.1. Stability of water-based lubricating fluid with nanoparticles

First of all, before dispersion, XRD was carried to test the nanoparticles. The result was shown in figure 2.

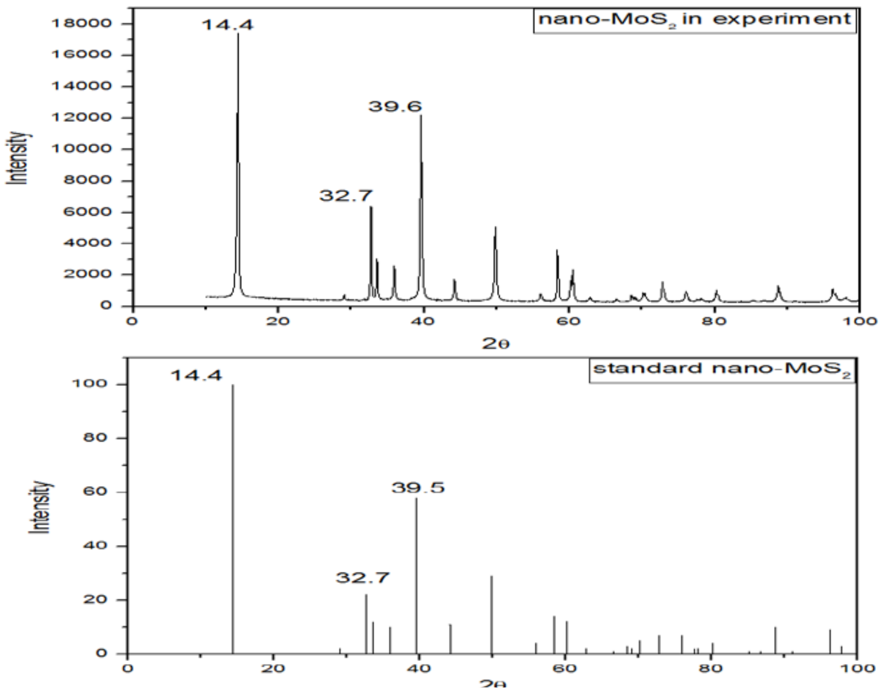

Figure 2. The XDR pictures of the nano-MoS_2 in experiment contrast to the standard nano-MoS_2.

The main diffraction peak of the experimental nano-MoS_2 is almost the same as the standard nano-MoS_2. It is demonstrated that the nanoparticles used in the experiments are nano-MoS_2. The Tecnai G20 FEI was used to measure the dispersion of nanoparticles before and after dispersion. The TEM diagrams were shown in figure 3. The particle size of MoS_2 particles is above 500 nm before dispersion, which shows that the particles aggregate largely at room temperature.

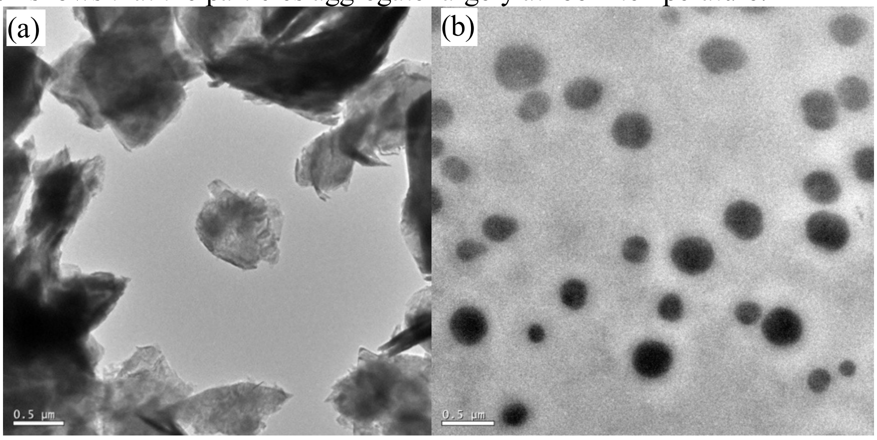

Figure 3. TEM images of undispersed nanoparticles (a) and dispersed nanoparticles (b) in room temperature.

From the figure 3(b), the sizes of the nanoparticles are mostly concentrated in the 100 nm-300 nm. The results show that the nanoparticles dispersion effect is ideal, and there is no large-scale agglomeration.

Then the Zeta potential of the solution was determined by using the Malvern Zetasizer Nano ZS. The three measurements were -44.7 mv, -45.4 mv and -46.4 mv, respectively. Since the absolute value of Zeta potential is greater than 30, the dispersion system is stability [16].

3.2. The last non-seizure value(P_B) of lubricating fluid

In the four-ball experiment, a point contact between the balls can be calculated accordingly to Hertz theory [17]. In the Hertz theory, the theoretical contact radius between two spheres is:

$$\alpha = \sqrt{\frac{3WR_1R_2}{4(R_1+R_2)}\left(\frac{1-\nu_1^2}{E_1}+\frac{1-\nu_2^2}{E_2}\right)} \qquad (1)$$

In the formula: ν is the Poisson coefficient of GCr15, E is GCr15 elastic modulus. Based on force analysis to top ball and bottom ball, contact force is 0.408 W, W represents the force, R=6.35 mm.

Table 1. Actual diameters of wear scars under different pressure after 10s testing and academic diameters.

Experimental force (N)	Actual wear spot diameter (mm)	Theoretical contact diameter (mm)
392	0.313	0.299
490	0.343	0.323
588	0.367	0.343
696	0.408	0.363
784	0.437	0.378
883	0.456	0.393
991	0.469	0.408

The theoretical results obtained by the Hertz theory are in the presence of no friction. As seen in the table 1, when the load is increased to 991 N, the difference between the actual grinding spot diameter and the theoretical contact diameter is only 13%. If the load is low, the actual grinding spot diameter will be equal to the theoretical contact diameter, which can lead to a conclusion that multilayer-MoS_2 nanoparticles have a good effect on wear and friction reduction. In case of a larger load, it can still maintain good wear and abrasion resistance. PB value of the 0.1% aqueous solution was determined under 559 N. However, compared with the solution without nanoparticles, the P_B value of the nano-lubricant is increased by 43%.

3.3. *Effects of nanoparticles on friction coefficient and surfaces of friction pairs*

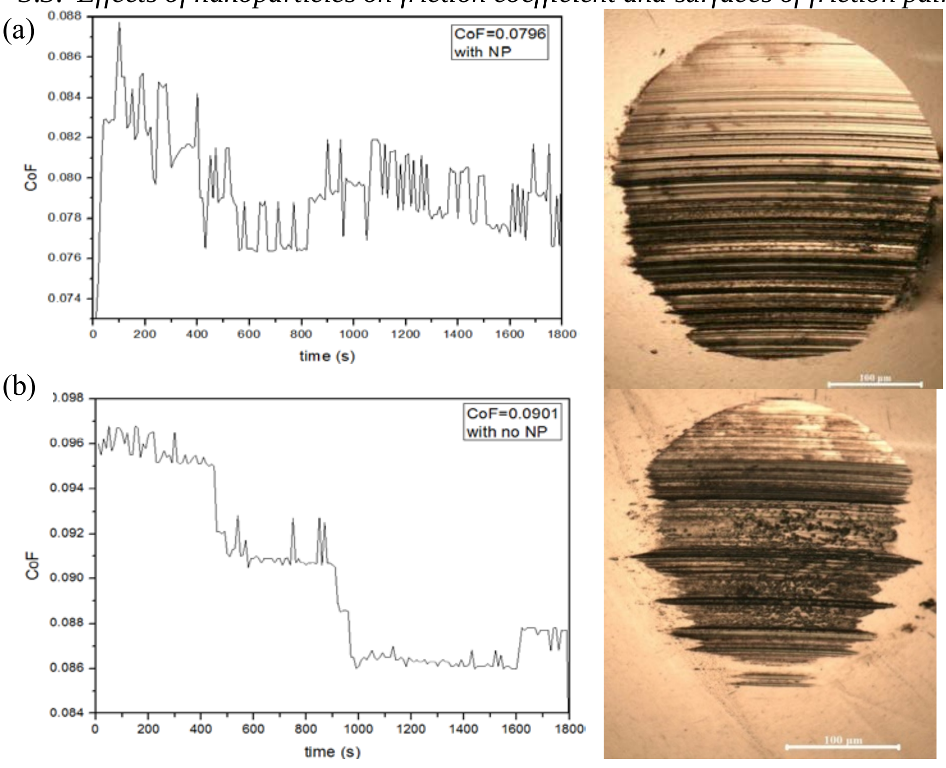

Figure 4. Time variation curves of friction coefficients and the corresponding surfaces of wear scars in water-based lubricating fluid with nanoparticles (a) and without nanoparticles (b) under 392N.

The determinations of friction coefficients of the water-based lubricants with nanoparticles and without nanoparticles were done under 392 N. Friction surfaces were observed after these tests. Time variation curve of friction coefficient and wear patterns are shown in figure 4.

After adding nanoparticles, the friction coefficients decrease significantly from 0.0973 to 0.0796. However, due to the friction in the process, the energy of the lubricants is increased, and the aggregation of nanoparticles occurs. If large particles attach to the surface of the friction pair, the friction coefficients will fluctuate. From the pictures of surfaces, it is obvious that the nanoparticles play an important role in reducing the grinding and greatly reducing wear and tear. In addition, friction surface is relatively smooth and no scratches appear.

3.4. Relationship between pressure and friction coefficients

Four-ball wear test machine under different experimental conditions with 1200 r/min rotating speed was used, and the friction coefficients of the lubricants standing after 1 day and 30 days were determined. The experimental data are as follows:

Table 2. Data of friction coefficient under different pressures.

Experimental force (N)	friction coefficient after 1day	friction coefficient after 30 days
392	0.079	0.090
490	0.078	0.084
588	0.066	0.067
696	0.067	0.069
784	0.069	0.071
883	0.061	0.064
991	0.064	0.067

From the table 2, the friction coefficients decreased with the increase of experimental force. Because the MoS_2 film layers are held together mainly by week Van der Waals force connection, they will slide under a smaller force. When the experimental force is increased, the sliding occurs between the slice layers, so the friction coefficients decrease [18].

The calculation results show that there is a sliding between the layers of MoS_2 nanoparticles. Each wear experiment requires 10g lubricant, which contains 0.01g nanoparticles. When the experimental force is 991 N, the average friction force is 7 N, and the line speed is 0.798 m/s, so the friction work is 5.686 J per second. The friction coefficients chart under 588 N is as follows:

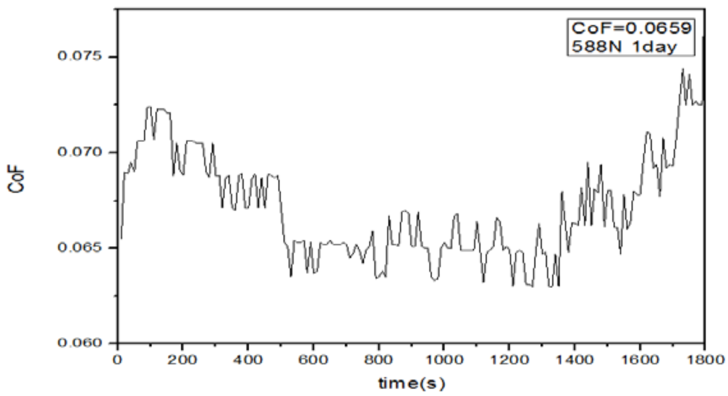

Figure 5. Relationship between friction coefficients and time under 588N.

From the pictures of friction coefficients under 392 N and 588 N, friction coefficients are larger at the beginning, because the beginning of friction produces a large number of new surfaces. The friction coefficients of the 500 s are suddenly reduced because MoS_2 particles begin to slide between the layers. Supposedly, there are only two MoS_2 layers in the nanoparticles. With the energy 76 KJ of the 1 mol nanoparticles, which greater than the maximum Van der Waals energy-hydrogen bond energy 40 KJ, the nanoparticles could slide at the beginning of friction. But the multilayer MoS_2nanoparticles are used in experiment. Therefore, the accumulation of energy needs to make all the MoS_2 layers sliding. 1mol MoS_2 particles work up to 45000 KJ energy for 500 s. Therefore, in the experiment, multilayer MoS_2 nanoparticles can overcome Van der Waals force of the layers to slide.

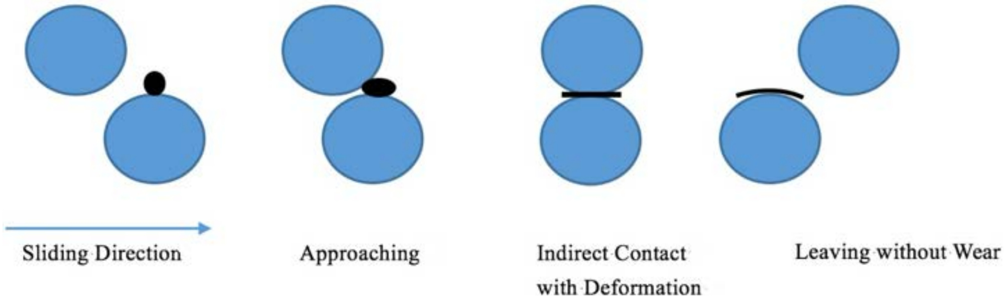

Figure 6. Diagram of the lubricating mechanism withMoS_2 nanoparticles.

With the friction time going on, the wear of the friction pair surfaces increase, and the friction coefficients increase with the accumulation of friction particles. With the friction process, the chances of contact between nanoparticles are increased so that agglomeration of nanoparticles is easy to occur to raise the friction coefficient. The following figures are three-dimensional morphologies of wear surface under the experimental force 883 N and 991 N after 30 min testing:

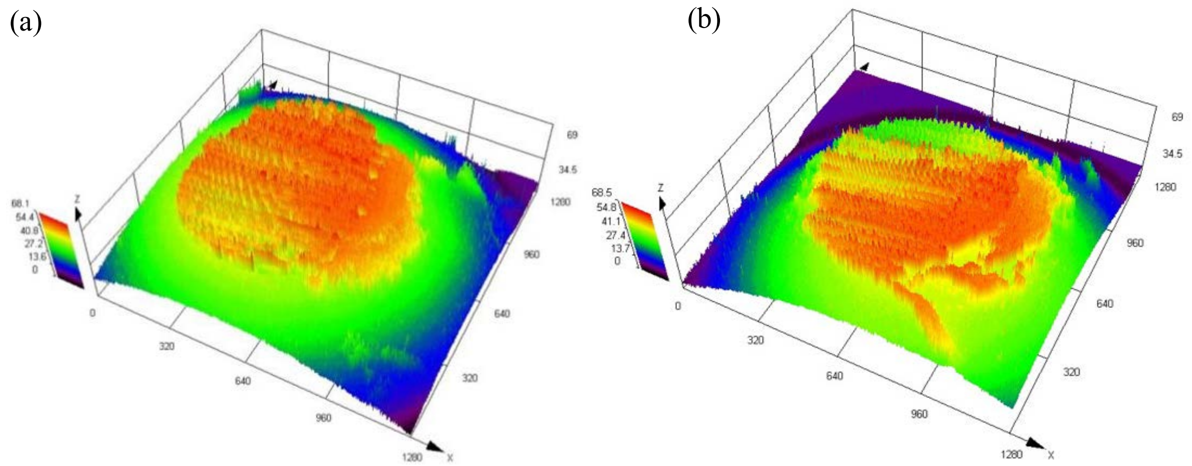

Figure 7. 3D-surface topography picture of wear scars under different pressure (a) 883 N (b) 991 N after 30 min testing.

From the morphologies, with the higher of pressure, the micro convex peaks on the surfaces of the friction pairs and the wear rate increase at the same time. Moreover, the distribution of oil film is no longer uniform under the high pressure of 991 N and grinding spot is not a complete round. The results confirm that the unstable and aggregation number of nanoparticles in the lubricating fluid of high pressure are increased, the oil film is partially damaged, resulting in poor lubrication effect. Under low pressure, the lubricating effect is ideal, the nanoparticles are not in a large scale, and the friction surfaces are smooth and the wear amount is small.

Under the experimental conditions of 588 N, the friction coefficients of the lubricating fluid after 1 day were measured at different speed. The changes of friction coefficients are shown in figure 8.

From the figure 8, with the faster of rotational speed, the friction coefficient has a tendency to decrease. High speed improves the thermal effect between the friction pairs, so the lubricant viscosity drop, lubricating effect is enhanced. In addition, when wear becomes slightly increase, a small amount of grinding particles play a role in lubrication, the friction coefficient decrease. But when the speed exceeds a certain value, the friction will destroy the integrity of the lubricating layer, so that the friction coefficients increase [20]. In the pace of the further aggravation of wear, wear particles accumulate, resulting in the third body friction, so that the friction coefficients increase. With the higher of rotational speed, the stable time of friction coefficients of lubricants is reduced. This is due to the decrease of the time with the increase of the rotational speed, which the lubricants are attached to the surface of the friction pairs. However, the high speed movement is not conducive to the adhesion of nanoparticles and the wear rate of both top ball and bottom ball is higher with more wear particles accumulation, so the friction coefficients increase slightly.

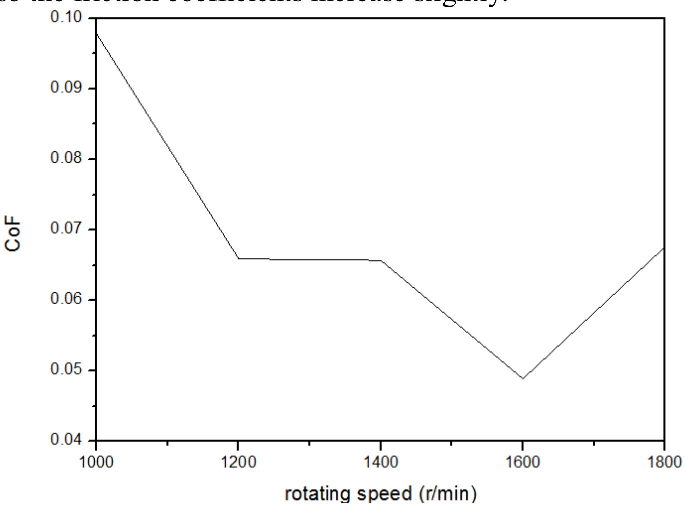

Figure 8. Graph of friction coefficients under different rotating speeds.

4. Conclusion

With the use of sodium dodecyl benzene sulfonate, 2, 2, 4-Trimethyl-1,3-pentanediol monoisobutyrate (cs-12)and sodium polyacrylate as dispersants, multilayer-MoS_2 nanoparticles are dispersed into oleic acid / triethanolamine water-based lubricants. Through the determination of MoS_2 particles' size in this lubricating liquid and Zeta potential, MoS_2 nanoparticles with smaller size can be stably dispersed in the solution, with no large-scale reunion, and dispersion effect is ideal.

After adding nanoparticles, the bearing capacity of water-based lubricating liquid is obvious improved. Under 883 N the lubricants still have good lubrication effect, and the solution can withstand the pressure of 5.9 GPa. The friction coefficients of water-based nano-MoS_2 lubricating fluid decrease with the increase of rotational speed. The yield strength of multilayer-MoS_2 nanoparticles is lower than that of singlelayer-MoS_2, but higher than the yield strength of the general steels, so it can provide good lubrication effects in the actual rolling process. The calculation results show that the low friction coefficients under high load are caused by the sliding between the layers of MoS_2 nanoparticles. The water-based lubricants can be used under the condition of high load and high speed in the actual production process. In the process of friction to 500 s or so, the lubricating fluid shows the best lubrication effect.

Nanoparticles as additives in the large particle size will have a scratch on the friction surface, causing fluctuations in the coefficient of friction, the short storage time and other issues arise. It is still a problem remains to be solved that how to stabilize the nanoparticles in water with smaller particle size in aneconomic, convenient and efficient way.

Acknowledgements

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