Tribological properties and lubricating mechanism of SiO$_2$ nanoparticles in water-based fluid

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Abstract. The tribological properties of surface modified SiO$_2$ nanoparticles suspension in water-based lubricant have been studied. SiO$_2$ (30 nm) nanoparticles were dispersed through surface modification with polyethylene glycol-200. Transmission electron microscope (TEM) and infrared (IR) spectroscopy show that SiO$_2$ nanoparticles disperse well and stably in the water-based lubricant. The diameter of the nanoparticles is about 60 nm. Tribological properties of the water-based lubricant were evaluated using four-ball wear test machine and pin-on-disk tester under different loads and different concentrations of SiO$_2$ nanoparticles. Wear surface morphology, element chemistry configuration of steel balls and steel rings were studied by means of X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Results show that the tribological properties of the water-based fluid have been improved by addition of nanoparticles ranging from 0.1% to 0.3% concentrations. SiO$_2$ nanoparticles deposited onto the wear surface during the sliding, which helped to reduce the friction coefficients and increase the anti-wear properties due to the miniature ball bearing effect and self-repairing performance of nanoparticles between the friction pairs. With the increase of test load, the friction coefficients decrease but the wear of the surface increase.

Keywords: SiO$_2$ nanoparticles, Tribological properties, Lubrication mechanism

1. Introduction

With the development of nanomaterials in lubrication technique and the deepening understanding of the particularity of nano-functional materials, nanomaterials have a broad application prospect in the field of metal processing lubrication with its unique physical and chemical properties. Using different additives to improve the tribological performance of lubricants is a widely used method [1-2]. With the researches of the nano-tribology gradual deepen, metal and oxide in nanoscale as functional additives in lubricants have been reported have good anti-wear, antifriction and extreme pressure performance, also have a certain of self-repairing function, as well as solving environmental problems of oil lubricants [3].

At present, there are many researches of water-based nano-fluid using in the lubrication, but the application of SiO$_2$ nanoparticles in water-based fluid are rarely reported. In this paper, a stably dispersed SiO$_2$ nanoparticles water-based fluid was obtained, with polyethylene glycol-200 as dispersants. Tribological performances of the water-based lubricants were evaluated using Four-ball friction and wear tester and pin-on-disk tester under different loads and different concentrations of SiO$_2$ nanoparticles. Wear surface morphology and element chemistry configuration of steel rings were studied by means of X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Results show that the tribological properties of the water-based fluid have been improved by addition of nanoparticles ranging from 0.1% to 0.3% concentrations. SiO$_2$ nanoparticles deposited onto the wear surface during the sliding, which helped to reduce the friction coefficients and increase the anti-wear properties due to the miniature ball bearing effect and self-repairing performance of nanoparticles between the friction pairs. With the increase of test load, the friction coefficients decrease but the wear of the surface increase.
analyzed by the means of optical microscope, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

2. Experimental

2.1. The preparation of water-soluble SiO2 nanoparticles
The surface modification process is described as follows: SiO2 nanoparticles (30 nm) were stirred for 5 minutes in 15% ammonia solution at room temperature and then dried in the oven at room temperature. After drying, nanoparticles were put in the aqueous solution of polyethylene glycol – 200, stirred for 30 minutes under 60 °C, the quality ratio of nanoparticles and polyethylene glycol – 200 was 1:1, then the mixture was placed in the ultrasonic disperser with frequency of 20 KHZ and scattered for 5 minutes, ultimately, a stably dispersed water-soluble SiO2 nanoparticles were obtained.

2.2. Tribological performance test
Two groups of water-based fluid were used to study the tribological performance of nanoparticles, one group without nanoparticles (base fluid), and the other was added with nanoparticles with the concentration varied from 0.1 wt.% to 0.5 wt.% The last nonseizure load (PB) of water-based fluid has been evaluated with four-ball wear test machine. According to the ASTM D2783, the spindle speed was 1760 r/min, and experiments were lasted for 10s at room temperature, GCr15 steel balls with the hardness of HRC 61 ~ 65 and the diameter of 12.7 mm were used. The friction and wear studies of water-based fluid were performed using pin-on-disk tester, the spindle speed was 300r/min and experimenting for 30 minutes at room temperature. The ring was made from 45 # steel, and the inside diameter was 16 mm, outside diameter was 31.7 mm, and the surface hardness was HB162. Before experiment, the surfaces were grinded on 2000 # sandpaper to ensure that the initial surfaces were all at the same. The chemical composition of 45 # steel was shown in Table 1. After the test, the samples were used for surface analysis after rinsing with petroleum ether. The morphology and element analysis of the samples were acquired by scanning electron microscope (SEM), and elements combining state and binding energy of the sample surface were evaluated by X-ray photoelectron spectrometer (XPS).

Table 1. Chemical composition of 45 # steel.

| Element | C          | Si        | Mn       | Cr     | Ni     | Cu     |
|---------|------------|-----------|----------|--------|--------|--------|
| Content/% | 0.42 ~ 0.50 | 0.17~0.37 | 0.50~0.80 | <0.25% | <0.30  | <0.25  |

3. Results and discussion

3.1. Characterization of water-soluble SiO2 nanoparticles

![Figure 1. Infrared spectra of surface modified SiO2 nanoparticles.](image)

![Figure 2. Transmission morphology of SiO2 nanoparticles.](image)
Figure 1 was the infrared spectra of SiO$_2$ nanoparticles. The bands close to 3424 cm$^{-1}$ correspond to the stretching vibration peak of O–H, the peaks of stretching vibration in the plane and antisymmetric stretching vibration at 2875 cm$^{-1}$ and 1350 cm$^{-1}$ show that CH$_2$ is present in the molecular structure, and the antisymmetric stretching vibration, symmetric stretching vibration and bending vibration of Si–O–Si are close to 1099 cm$^{-1}$, 837 cm$^{-1}$ and 571 cm$^{-1}$. The weak band at 950 cm$^{-1}$ corresponds to the characteristic stretching vibration of Si–O–C [4]. According to the infrared spectrum of SiO$_2$ nanoparticles [5,6], there were stretching vibration peak of Si–OH at 2300 cm$^{-1}$, which didn't seen in figure 1. Thus the infrared spectrum of the samples indicates that the Polyethylene glycol-200 adsorbed on the surface of the SiO$_2$ nanoparticles by condensation reaction, which result in homodisperse of SiO$_2$ nanoparticles. The transmission morphology of surface modified SiO$_2$ nanoparticles (0.1 wt.%) is presented in figure 2. It can be seen that SiO$_2$ nanoparticles is amorphous and the average diameter is about 50 nm, and also the SiO$_2$ nanoparticles dispersed evenly in water, which confirms that nanoparticles were dispersed successfully.

3.2. Effect of the concentration of SiO$_2$ nanoparticles

Figure 3 shows the $P_B$ and friction coefficients of water-based fluid with varying concentration of SiO$_2$ nanoparticles. According to figure 3, it can be seen that the $P_B$ increased first but then decreased with the increasing concentration of SiO$_2$ nanoparticles, and reached the top of 883 N at 0.3 wt.% SiO$_2$ nanoparticles. In addition, the $P_B$ of water-based fluid which contains SiO$_2$ nanoparticles were improved obviously than that with base fluid, and the minimum increase is 13%. This is mainly because that the size of nanoparticles is small and well dispersed in the base fluid. In the process of sliding, nanoparticles easily entered into the friction pair, which prevents direct contact of friction pair, and the bearing capacity of water-based fluid is highly improved because of the high hardness of nanoparticles [7]. When the concentration of nanoparticles is more than 0.3 wt.%, SiO$_2$ nanoparticles would produce irreversible agglomeration which will result in the increases of particle size, reducing the amount of the nanoparticles entering into the friction pair, thus reduce the bearing capacity of water-based fluid.

![Figure 3. $P_B$ and friction coefficients of water-based fluid with varying nanoparticle concentration.](image-url)

The variation of friction coefficients with the increasing concentration of SiO$_2$ nanoparticles was plots in figure 3, which illustrates that the friction coefficients decrease when concentrations of SiO$_2$ nanoparticles are less than 0.3 wt.%, while increase when concentrations exceed 0.3 wt.%, the minimum value of friction coefficients is 0.154, reduced by 28% compared with the base fluid. Besides, the friction coefficients of water-based fluid with addition of nanoparticle were all less than that of base fluid. Accordingly, SiO$_2$ nanoparticles have good anti-friction performance, it’s contributes to the miniature ball bearing effect of SiO$_2$ nanoparticles, which changed the friction conditions from sliding friction to rolling friction, thereby reduce the friction coefficients [8,9]. When
the amount of SiO₂ nanoparticles was exceed 0.3 wt.%, the probability of nanoparticles forming agglomeration will increase, which made it difficult to get into the friction pair, and the larger particles lead to the surface scratched, leading to the friction coefficients increase [10].

Figure 4. Wear surface morphology of steel rings lubricated under water-based fluid with (a)base fluid, (b)0.1 wt.% SiO₂, (c)0.2 wt.% SiO₂, (d)0.3 wt.% SiO₂, (e)0.4 wt.% SiO₂, (f)0.5 wt.% SiO₂.

Figure 4 presents the wear surface morphology of steel rings lubricated under water-based fluid with different concentrations of nanoparticles. In figure 4(a), there were many scratches, and the scratches were intensive and deep. What’s more, two furrows were observed, indicating that the surface was severely weared when lubricated with base fluid. While when adding nanoparticles, the wear surfaces were more smooth and had less furrows compared with that of base fluid. When the nanoparticles content was more than 0.3 wt%, the number of scratches became more, more pits were also observed compared with figure 4(c), (d), nonetheless, the wear surfaces were better than that lubricated with base fluid. The reasons will be discussed in the mechanism of lubrication.

3.3. Influence of the test load

Figure 5. Friction coefficients of water-based.

The friction coefficients of water-based fluid with 0.3%wt and 0.5 wt.% SiO₂ nanoparticles under different test load were shown in figure 5. We can see that with the increase of test load, the friction coefficients were decreased, and the difference of friction coefficients between two kinds of water-
based fluid were becoming smaller. This phenomenon will be discussed in detail in the following section. The wear surface morphology lubricated with 0.5 wt.% SiO$_2$ nanoparticles water-based fluid under different pressures were shown in figure 6. Scratches became wider and the pits on the wear surface were disappeared with the increase of test load. In addition, there were adhesive wear and plough wear in figure 6(b), (c) and (d).

![Figure 6. Wear surface morphology under Nano-rolling fluid under different test load. (a) 200N, (b) 300N, (c) 400N, (d) 500N.](image)

3.4. Inquiry of lubrication mechanism

Wettability of lubricants reflects the adsorption and spreading performance of lubricants on the work piece and roll surface, therefore, it is necessary to discuss the effect and mechanism of nanoparticles on wettability. Figure 7 plots the influence of nanoparticles concentration on the wettability of water-based fluid, which are corresponding to 0, 0.1 wt.%, 0.3 wt.% and 0.5 wt.% nanoparticles respectively. The figures show that with the increase of nanoparticle concentration, the contact angle of water-based fluid was decreased. The higher concentration of nanoparticles, the easier water-based fluid adsorbed and spread on the metal surface, which is mainly because nanoparticles have high surface energy. With the addition of nanoparticles, the surface energy of the base fluid is reduced, the same with surface tension, therefore make the contact angle decrease. In addition, there are a large number of hydroxyl groups in the surface of nanoparticles, which easily adsorbed on the metal surface, making the adsorption increase and the contact angle decrease.

In order to study the mechanism of SiO$_2$ nanoparticles as water-based additives, the EDS and XPS of the wear surface under 0.5 wt.% SiO$_2$ nanoparticles were analyzed. The elemental composition and typical chemical state of element analysis results were shown in figure 8 and figure 9 respectively. Seen from the figure 8, the element of silicon was detected on wear surface, which illustrated that nano-SiO$_2$ were filled in the defects. The figure 9 showed there were two peaks at the binding energy of 102.7 eV for silica and 532 eV for oxygen, which were belong to the chemical state of SiO$_2$[11,12]. It showed that there was no reaction of SiO$_2$ nanoparticles, which were just deposited on the surface of the samples.
There are many lubricating mechanisms of nanoparticles as additives of lubricant have been proposed, such as the rolling friction mechanism, the formation of protective film, third-body effect and so on [13].

Figure 7. Influence of nanoparticle concentration on the wettability of water-based fluid.

Figure 8. EDS spectra of worn surface lubricated with 0.5 wt.% SiO₂ nanoparticles. (a) 200N, (b) 300N.

Figure 9. XPS spectra of the wear surface lubricated with 0.5 wt% SiO₂ nanoparticles with concerning element. (a) Si2p, (b) O1s (200N)

The lubrication principle is proposed as follows, under the high contact load, the based fluid and nanoparticles were penetrated into the friction pair and thus forming a thin physical lubricating film [14]. This lubricating film possesses a lot of important functions, such as avoiding direct contact by separating the friction pair, and bearing the load [15]. Besides, spherical nanoparticles are most likely to roll between the friction pair and reduce the friction coefficients [16,17]. Figure4 showed that, with the increase concentration of nanoparticles, the scratches became less and shallow, and the wear of surface was decreased. The reasons can be summed up in the following two points: Firstly, the “miniature ball bearing” effect of SiO₂ nanoparticles turn a part of sliding friction into rolling friction, thus reduce the wear of surface; Secondly, there are nanoparticles in the defects of figure 4(e), (f), proving that nanoparticles can deposit in the defects and repair the surface, thereby reducing the wear of surface. Interestingly, the wear of surface become serious when the concentration is more than 0.3 wt%, due to the agglomeration of nanoparticles, which causing surface scratched and particle deposition. As shown in Figure6, scratches became wider and the pits on the wear surface were disappeared with the increase of test load. What is more, there were adhesive wear and plough wear on the surface, but the scratches become wider and wear surface roughness was decreased. However, the effect of nanoparticles during sliding depends on the thickness of the lubricant film. Assumed that the
shape of nanoparticles is preserved, when the film thickness is close to the size of nanoparticles, rolling friction is considered to be the leading mechanism [18].

As shown in figure 6, with the increase of test load, there were obvious furrows in wear surface, indicating that nanoparticles did not melt, and the shape of nanoparticles was preserved. With the increase of test load, the thickness of lubricant film decreases. When test load is small, the lubrication film is denser, which plays an important role in lubrication; while with the increase of test load, the thickness of lubrication film would decreased. When the thickness was approach to the size of nanoparticles, the nanoparticles would plays a major role in lubricant, making rolling friction become the main mechanism, thus reducing the friction coefficient, on the other hand, the increasing of test load would reduce agglomeration of nanoparticles, thus making the effect of nanoparticle concentration on the friction coefficients decreases. But because of the increasing load, nanoparticles embedded into the sample surface, making the surface wear heavier.

4. Conclusion
SiO₂ nanoparticles modified by polyethylene glycol-200 were well dispersed in water-based fluid through condensation reaction.

Carrying capacity and antifriction performance of the base fluid can be improved by adding nanoparticles when the concentration of nanoparticle is less than 0.3 wt%. The optimal concentration of SiO₂ nanoparticles is 0.3 wt%. If excess nanoparticles are added into the base fluid, SiO₂ nanoparticles would tend to form irreversible agglomeration, which will result in worse friction.

With the increase of test load, antifriction performance of SiO₂ nanoparticles has been improved, while the antowe performance is decreased.

Tribological performance of the base fluid are improved mainly by the “miniature ball bearing” effect and self-mending effect of SiO₂ nanoparticles, when the test load increase, the thickness of lubrication film decreases and nanoparticles plays a main role in lubrication, nanoparticles embedded into the sample surface which increasing the wear of surface.

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