J Nanopart Res (2011) 13:2129–2137
DOI 10.1007/s11051-010-9970-x

RESEARCH PAPER

Friction and wear properties of ZrO_2/SiO_2 composite nanoparticles

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Received: 3 March 2010 / Accepted: 22 May 2010 / Published online: 15 June 2010

Abstract In this article, the lubrication properties of ZrO_2/SiO_2 composite nanoparticles modified with aluminum zirconium coupling agent as additives in lubricating oil under variable applied load and concentration fraction were reported. It was demonstrated that the modified nanoparticles as additives in lubrication can effectively improve the lubricating properties. Under an optimized concentration of 0.1 wt%, the average friction coefficient was reduced by 16.24%. This was because the nanoparticles go into the friction zone with the flow of lubricant, and then the sliding friction changed to rolling friction with a result of the reduction of the friction coefficient.

Keywords ZrO_2/SiO_2 · Additive · Friction · Self-repairing · Lubrication · Colloids

Introduction

As the viscosity of a lubricant decreases, the frictional force in the hydrodynamic lubrication regime decreases. The decrease of the lubricant viscosity causes a lower extreme pressure of the lubricant, so the friction surface is damaged at high load due to the metal contact, which makes reliability worse (Lee et al. 2009). With the development of nanostructured materials in the recent years, attempts were made to use nanoparticles as lubricant additives to improve their lubrication properties (Song and Zhang 2008). When some nanoparticles were added into the lubricating oil, their lubrication properties can be effectively improved (Red'kin 2004; Hu and Dong 1998; Dong et al. 1998; Guo et al. 2009), which is better than the traditional solid lubricant additives and becomes a promising new lubricating material. A previous study revealed that nano-lubricant which was a mixture of nanoparticles and lubricating oil increased the extreme pressure of the lubricant and reduced the friction coefficient, which could make the bearing more durable (Kwangho et al. 2009; Murakami et al. 2007). Zhang et al. (2009) reported that using $CaCO_3$ nanoparticles as PAO base oil additives can dramatically improve the load-carrying capacity, as well as the anti-wear and friction reduction properties of PAO base oil. In addition, higher applied load, moderate frequency, longer duration time, and lower temperatures were beneficial to the deposition of $CaCO_3$ nanoparticles accumulating on rubbing surfaces. Jee and Lee (2009) showed that the surface-functionalized diamond nanoparticles were highly dispersive and stable in oil, and can be used as lubricating oil additives without further modifications.

It has been reported that the main mechanism of the friction reduction when nanoparticles were added can be attributed to rolling/sliding effect (Wu et al. 2007; Chin-as-Castillo and Spikes 2003), protective

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film (Hu et al. 2002; Zhou et al. 2007), third-body effect (Rapoport et al. 2003), and mending effect (Liu et al. 2004). It is also found that there are different interactions when two or more nanoparticles lubricant additives are added, such as adduct effect, synergy, and antagonism effects (Sui et al. 2009). Although these effects have obvious influence on the performance of lubricating oil when nanoparticles were used as additives, the present study is few and highly needed.

In this article, ZrO_2/SiO_2 composite nanoparticles were prepared with in situ modified method and surface was modified by aluminum zirconium coupling agent. Such modified ZrO_2/SiO_2 nanoparticles showed good dispersion stability in the lubricant. In order to estimate the ranges of application of ZrO_2/SiO_2 composite nanoparticles used as lubricating oil additive, the friction test was designed by four balls tester. The lubricative properties of ZrO_2/SiO_2 composite nanoparticles as additives in lubricating oil under variable load and concentration fraction were evaluated. In addition, the possible lubrication and anti-wear mechanism was discussed.

Experimental

The superficial modification of ZrO_2/SiO_2 composite nanoparticles

Zirconium acetate was added to 100 mL alcohol (95%) and heated stirring to form a sol. The pH value was set at 9–10 by ammonia dropping. After three times washing with alcohol (95%), ZrO_2 precursor was prepared; 0.025 mol TEOS was added to 100 mL alcohol (95%), then the ZrO_2 precursor was added. Next 0.026 g ammonium hydrogen fluoride was added and heated stirring to form a sol. The pH value was set at 9–10 by ammonia dropping. After three times washing with alcohol (95%), ZrO_2/SiO_2 precursor was prepared; the ZrO_2/SiO_2 precursor was dissolved with 150 mL alcohol (95%). The aluminum zirconium coupling agent was added and the concentration was 0.6 wt%. The solution was mixed 1.5 h before put into the autoclave. The reaction conditions were set as follows: temperature 220 °C, pressure 3.6 MPa, time 2 h. The powder was put out until the reactor cooled to room temperature. Then the modified ZrO_2/SiO_2 composite nanoparticles were made. Such modified ZrO_2 particles and SiO_2 particles were homogenously mixed together. The interaction between the nanoparticles achieved the best. The composite nanoparticles particle size, morphology, and modification effect were observed with transmission electron microscopy (TEM) and Zeta potential analyzer. The absorbency of nano-oil was measured with an ultraviolet spectrophotometer.

Anti-wear friction test

The anti-wear friction properties were tested by a four balls tester (MMU-10G, Jinan). The modified ZrO_2/SiO_2 composite nanoparticles were added into lubricating oil (#20) under different concentration fraction (mass concentrations were: 0, 0.05, 0.1, 0.3, 0.5, 0.75, and 1 wt%). For each concentration, the fraction coefficients were measured five times and then averaged to ensure the data accuracy. The oil solution was dispersed with ultrasonic for 30 min and then nano-oil was obtained. The operation process was shown in Fig. 1. Then the nanoparticles were homogenously dispersed in the lubricating oil. The nano-oil was kept at room temperature for 48 h. Then wear friction and wear tests were performed with a four balls tester. The experimental data was recorded in situ and the test data were acquired with a computer automatically.

Four-ball friction and wear test

In four-ball friction process, the three balls located below were tightly fixed, as shown in Fig. 2. The top

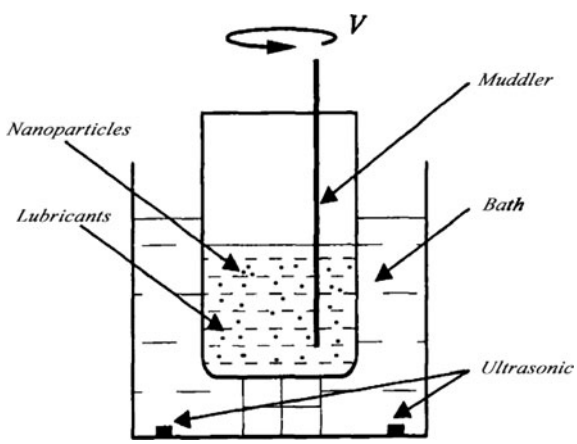

Fig. 1 Preparation setup and process of the nano-oil measured in this article

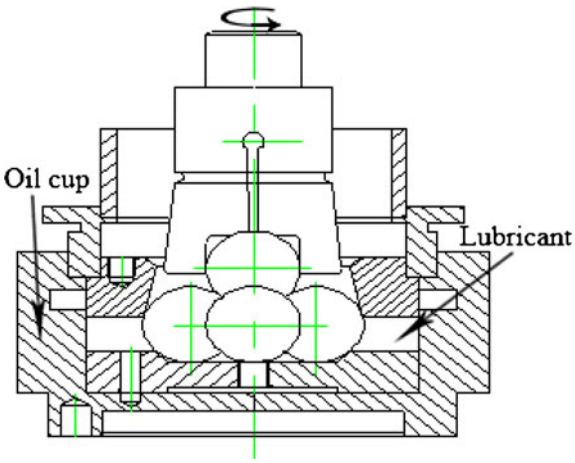

Fig. 2 The structural sketch map of four-ball friction and wear test

ball was driven and rotated on the three supporting balls. Four-ball wear test parameters were set as follows: temperature at 75 °C, speed of 1,450 r/min, load at 147 N, and time of 30 min. The ball was in accordance with the steel ball GB/308-89 manufacturing, GCr15, two steel balls, diameter 12.7 mm; hardness 64-66HRc. Friction coefficient was recorded by the data terminal processing systems. The size of wear scar diameter was observed with a metallographic microscope and then the average size of wear scar diameter was obtained.

Thrust ring friction and wear test

In thrust ring friction process, the test loop was suspended in order to push the ring in the form of surface contact friction, as shown in Fig. 3. The friction coefficient, wear volume and changes in surface morphology of friction pairs were obtained. After each experiment, the surface of friction pair was washed with petroleum ether, so that there were no impurities on the surface and the quality changes were accurately measured. Friction coefficient was recorded by the data terminal processing systems. The wear quality changes were recorded by the electronic balance. The friction pair surface morphology was observed with SEM. Thrust ring wear test parameters were set as follows: temperature at 75 °C, speed of 1,200 r/min, load at 200 N, and time of 30 min. The thrust ring is 45 # steel, hardened to 45-50HRC, outside diameter of 50 mm, inner

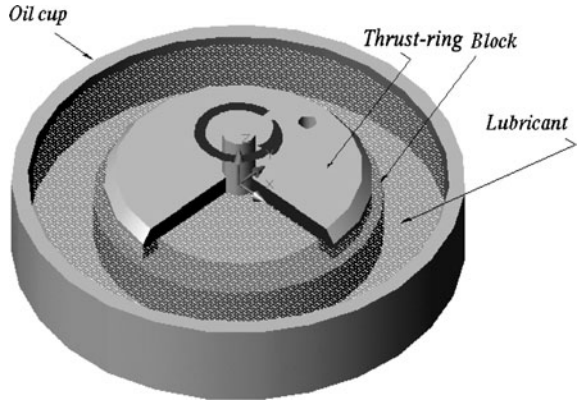

Fig. 3 The structural sketch map of thrust ring friction and wear test

diameter of 42 mm, and thickness of 5 mm; test ring is 45 # steel, hardened to 44-46HRC, outside diameter of 54 mm, inner diameter of 38 mm, and thickness of 10 mm.

Results and discussion

Effect of surface modification

Dispersibility stability analysis

The agglomerating between nanoparticles was characterized with the Zeta potential value. The bigger absolute value means the nanoparticles disperse more homogenously. The absolute value of ZrO_2/SiO_2 Zeta potential was shown in Fig. 4. As shown in Fig. 4, Zeta potential absolute value of modified ZrO_2/SiO_2 nanoparticles was greater than that of as-prepared ZrO_2/SiO_2 nanoparticles. This indicated that static repellency of modified ZrO_2/SiO_2 become stronger than the as-prepared nanoparticles. The modified ZrO_2/SiO_2 was well dispersed in lubricating oil.

Figure 5 is the TEM image of the ZrO_2/SiO_2 composite nanoparticles. As shown in Fig. 5a, some ZrO_2/SiO_2 nanoparticles agglomerated. However, the modified nanoparticles were well dispersed and their sizes were rather uniform of 50–80 nm. The distribution of large particles was less, almost no agglomeration, as shown in Fig. 5b. It was demonstrated that the specific surface area of the modified ZrO_2/SiO_2 composite nanoparticles was reduced significantly, and the surface activity was also decreased. Finally,

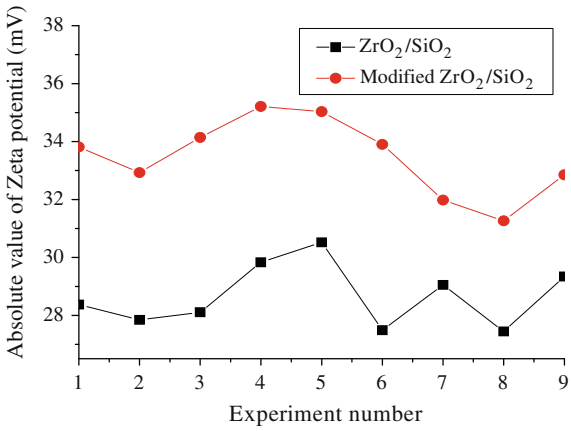

Fig. 4 The absolute value of ZrO_2/SiO_2 nanoparticles Zeta potential

the aggregation of the nanoparticles was effectively inhibited. The dispersion stability of nanoparticles was greatly enhanced.

Oil-soluble analysis

The ZrO_2/SiO_2 nanoparticles were added into lubricating oil and then the absorbency of nano-oil with time was observed by ultraviolet spectrophotometer, as shown in Fig. 6. The absorbency should be greater if the dispersion of nano-oil is better. After 56 h, the absorbency of nano-oil with modified ZrO_2/SiO_2 nanoparticles was still stable. However, the nano-oil with as-prepared ZrO_2/SiO_2 nanoparticles showed some precipitates. The absorbency showed decreasing of 3.5% in 76 h for functionalized particles, but 7% for as-prepared particles. The modified ZrO_2/SiO_2 nanoparticles can steadily disperse in lubricating oil. The images shown in Fig. 7 were taken after the oil was kept at room temperature for 12 h. As can be seen from Fig. 7a, the as-prepared ZrO_2/SiO_2 nanoparticles precipitated at the bottom of the bottle. However, the modified ZrO_2/SiO_2 nanoparticles were well dispersed in the oil (Fig. 7b). This because that the surface of nanoparticles changed from inorganic phase to organic phase. This was due to that aluminum zirconium coupling agents bond with the ZrO_2/SiO_2 composite nano-particle surface hydroxyl. The role mechanism was shown in Fig. 8. The surface of ZrO_2/SiO_2 composite nanoparticles was successfully modified.

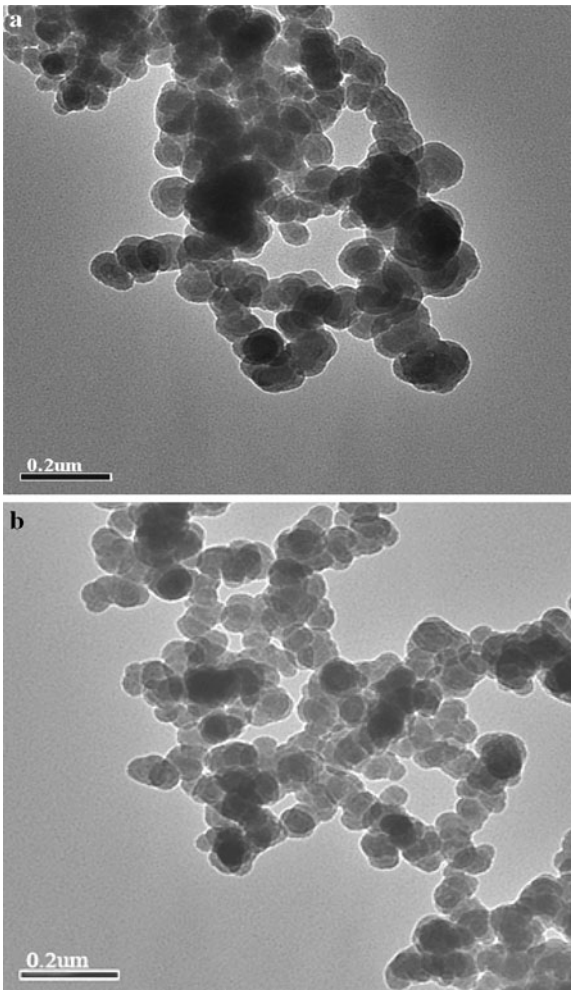

Fig. 5 The TEM image of ZrO_2/SiO_2 composite nanoparticles. **a** As-prepared ZrO_2/SiO_2 nanoparticles and **b** modified ZrO_2/SiO_2 nanoparticles

Friction and wear test

Four-ball test friction coefficient analysis

Figure 9 showed friction coefficient changes with the concentration fraction of ZrO_2/SiO_2 composite nanoparticles in lubricant oil. The friction coefficient decreased with the ZrO_2/SiO_2 concentration increased when the concentration was <0.1 wt%. However, the coefficient began to increase when the additive concentration was >0.1 wt%, as shown in Fig. 9. The reason was that, due to the flash temperature caused by the friction, the nanoparticles

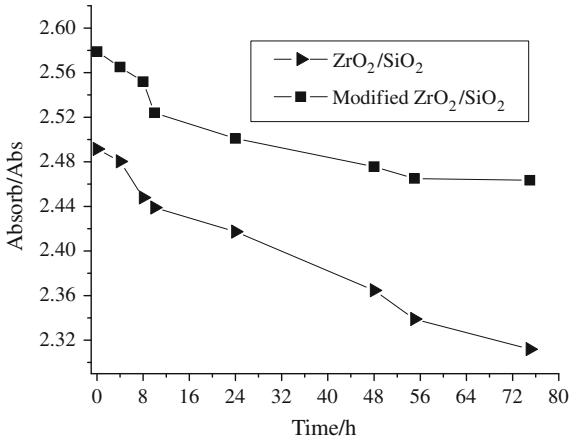

Fig. 6 The absorbency curve of nano-oil with time

adsorbed chemically on the metal friction surface through hydroxyl (Hu et al. 1998; Sun et al. 2002; Merschdorf 2002). At the same time, nanoparticles go into the friction zone with the flow of lubricant. Then the sliding friction was changed into rolling friction between the friction pair (Xu et al. 1997) with the result of the reducing friction coefficient. The lubrication mechanism was shown in Fig. 11. When fewer nanoparticles were added, e.g., 0.05 wt%, the friction zone cannot be completely filled. Therefore, the ball bearing effect cannot play and anti-friction effect was not obvious. When more nanoparticles were added, e.g., 0.5 or 1 wt%, nanoparticles were sintered into blocks by friction. Therefore, larger nanoparticles as impurities scratched the friction surface and the friction coefficient increased. Therefore, only when the added amounts of nanoparticles were in an optimal concentration range, the friction-reducing effect is better. As shown in Fig. 10, the friction-reducing effect was more effective at the additivities concentration of 0.1 wt% with an average friction coefficient decreasing of 16.24%.

Four-ball test wear scar diameter analysis

Table 1 showed the diameter of wear scar on the balls in the lubricant oil with different concentration of nanoparticles. When the concentration was 0.1 wt%, the average size of wear scar diameter was the smallest. Figure 12 compares the wear scar morphologies of ball in lubricant oil with and without of the ZrO_2/SiO_2 nanoparticles. When no nanoparticles

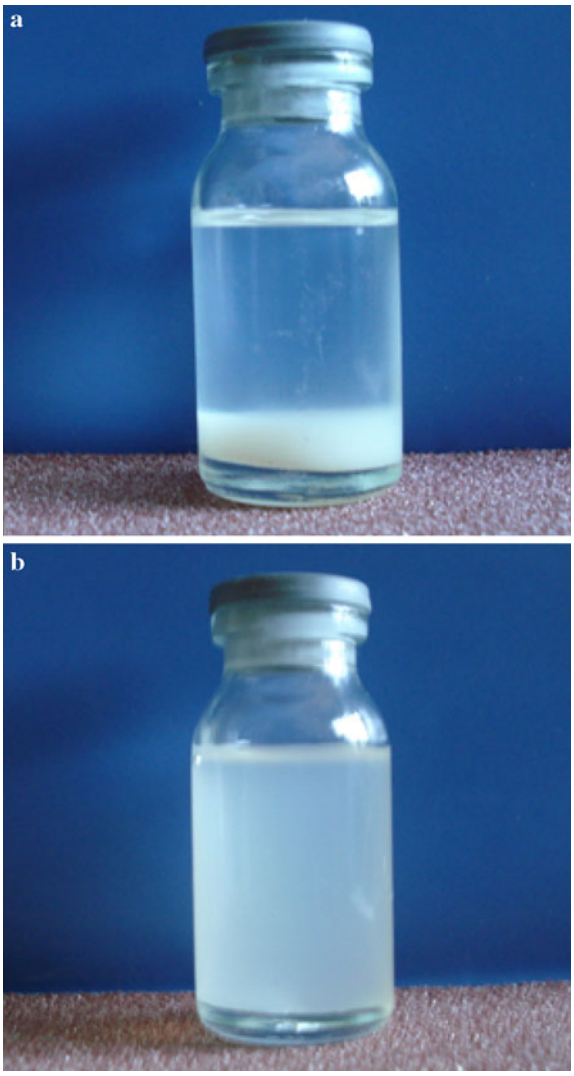

Fig. 7 The images of oil solution with different nanoparticles after 12 h. **a** With as-prepared ZrO_2/SiO_2 nanoparticles and **b** with modified ZrO_2/SiO_2 nanoparticles

were added, the vertical wear scar diameter of ball was 422.37 μm, as shown in Fig. 12a. Also the wear scar was deep and furrow from the existence of wear and tear rather than the elastic deformation. However, when the additivities concentration was 0.1 wt%, the longitudinal wear scar diameter was 360.73 μm, as shown in Fig. 12b. While wear scar diameter was reduced by 61.64 μm, reduced the rate of 14.59%. These showed that the lubricating oil by adding a certain amount of modification ZrO_2/SiO_2 composite nanoparticles could play well anti-wear effects in the friction pairs (Kato and Komai 2007).

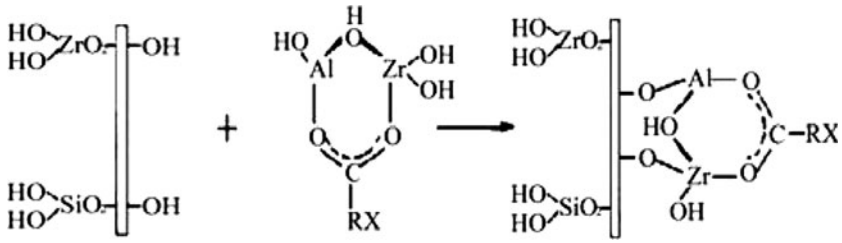

Fig. 8 The role mechanism of aluminum zirconium coupling agent

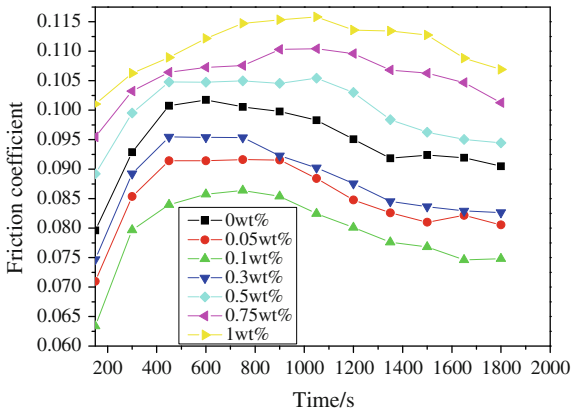

Fig. 9 Variation of friction coefficients with times in four-ball test

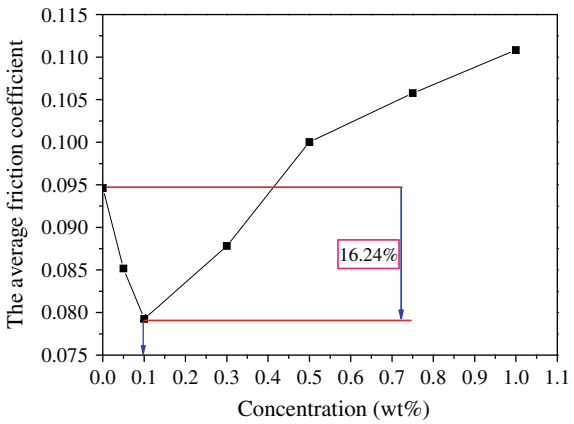

Fig. 10 Variation of the average friction coefficients with concentration fraction

Thrust ring wear test quality analysis

Table 2 showed the average mass loss of the thrust ring after the wear test when ZrO_2/SiO_2 additivities of different concentration were used. The weight loss decreased with the ZrO_2/SiO_2 concentration increases when the concentration was <0.1 wt%. However, the

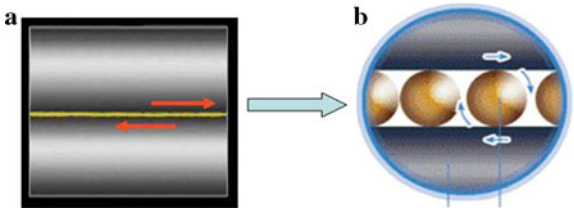

Fig. 11 The micro image of lubrication mechanism. **a** Sliding friction and **b** rolling friction

Table 1 The diameter of wear scar of the balls dispersed in the oil with different concentration of nanoparticles

	1	2	3	4	5	Average (μm)
0 wt%	422.37	421.68	421.35	422.96	423.49	422.37
0.05 wt%	380.89	381.02	380.96	379.26	379.17	380.26
0.1 wt%	360.40	361.35	360.73	359.64	361.53	360.73
0.3 wt%	386.97	385.99	386.51	385.24	386.99	386.34
0.5 wt%	430.93	429.24	429.83	431.03	429.82	430.17
0.75 wt%	432.26	433.89	434.02	433.54	431.74	433.29
1 wt%	439.12	438.96	440.12	439.79	441.06	439.81

weight loss began to increase when the additive concentration was >0.1 wt%, which was consistent with Figs. 9 and 10. In addition, when the nanoparticles adding amount was 0.1 wt%, the negative wear and tear was obtained. It can be explained with the dynamic self-healing deposition mechanism (Song and Zhang 2006). That was, mass loss caused by friction and nanoparticles deposition onto the friction pair surface coexisted. When the wear and tear was faster than the deposition, the mass lost happened. Otherwise, the thrust ring mass increased. When the concentration of ZrO_2/SiO_2 composite nanoparticles was 0.1 wt%, the performance of negative wear and tear was observed, which was caused by the dynamic self-healing mechanism of deposition, as shown in Fig. 13.

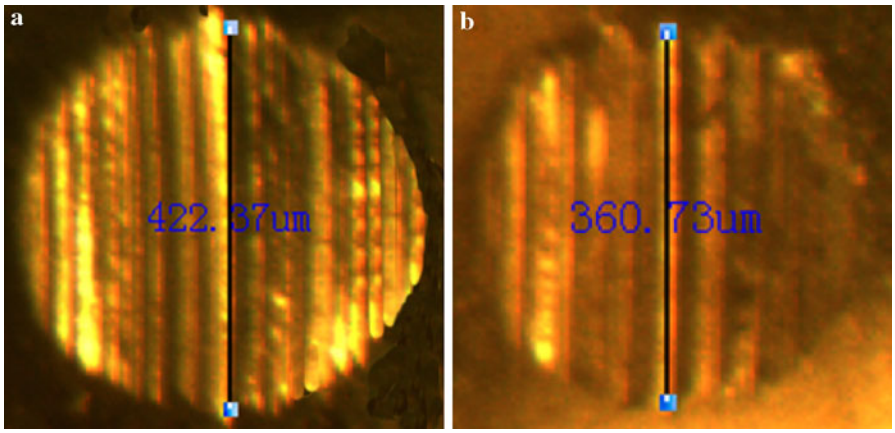

Fig. 12 Wear scar morphology of four-ball test (60×). **a** Lubricated by #20 mechanical oil with 0 wt% ZrO_2/SiO_2 and **b** lubricated by #20 mechanical oil with 0.1 wt% ZrO_2/SiO_2

Thrust ring test friction surface analysis

Figure 14 shows the SEM image of the thrust ring friction surface. As can be seen from Fig. 14a, when the lubricating oil without additives was used in the friction tests, noticeable scratches and furrows were clearly observed on the thrust ring surface. However, when ZrO_2/SiO_2 composite nanoparticles of 0.1 wt% were added into the same lubricating oil, the furrows were much shallower and narrower, as shown in Fig. 14b. At the same time, some white nanoparticle sediments were observed on the surface, which were filled into the scratches as indicated in the white box of Fig. 14b. It meant that some composite nanoparticles deposited onto the friction surface during the friction process.

Due to the small nanoparticle size, they can easily move into the worn area under the compressive stress of lubricating oil. Then a self-laminating film was formed on the friction surface, which can repair the surface (Huang et al. 2006). Moreover, low-energy electrons were released into lubrication medium during the friction process, and the positive and negative electric charge was produced in the friction pair's surface. Then, the released electrons combined with the chemical additives and anions or free radicals were formed, $M + e \rightarrow (MR) + {}^{+}R$. Finally, free radical R covered the friction pair's surface with silicon dioxide or zirconium. Therefore, the nanometer granule became protective film in the friction pairs face shape under this physical chemistry dual function (Merschdorf 2002). The forming mechanism was schematically shown in Fig. 15. This layer existed in solid state after the friction, and repaired dent friction surface. As can be seen from Fig. 14b, surface scratch of thrust ring changed smooth. The plow furrow was shallow, and the surface had the white deposit to appear.

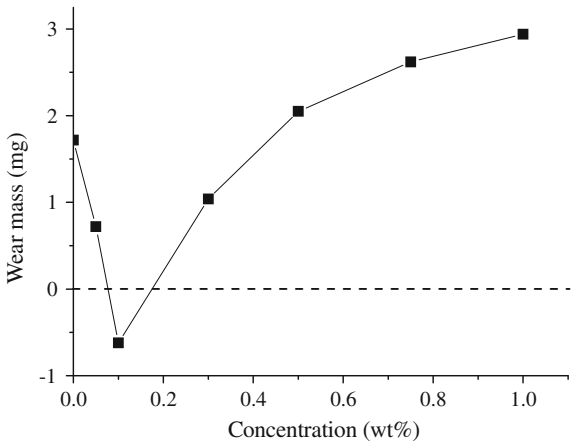

Fig. 13 Variation of the average wear mass with concentration fraction

Table 2 The average weight mass of the thrust ring

Concentration	0 wt%	0.05 wt%	0.1 wt%	0.3 wt%	0.5 wt%	0.75 wt%	1 wt%
Wear mass (mg)	1.72	0.72	−0.62	1.04	2.05	2.62	2.94

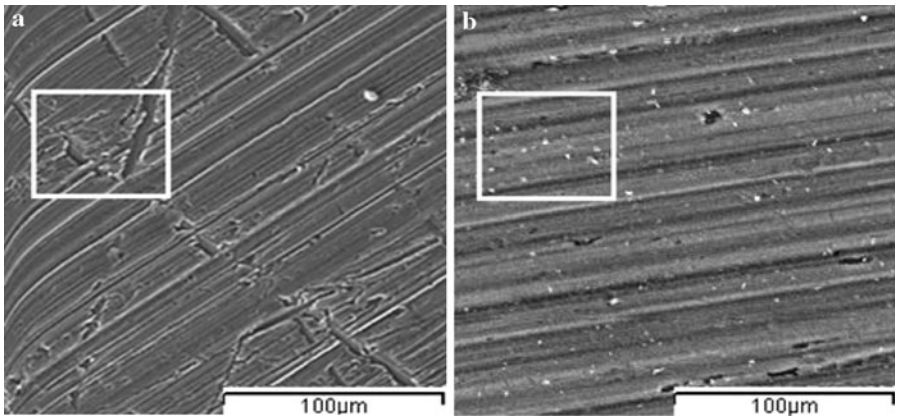

Fig. 14 The morphology of the wear scar on ring-on-block test. **a** Ring (0 wt%) and **b** ring (0.1 wt%)

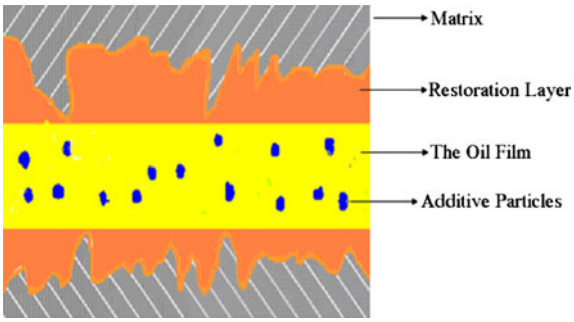

Fig. 15 The forming mechanism of self-laminating film on friction pair

Conclusion

In this article, the enhanced lubrication properties of lubricating oil with ZrO_2/SiO_2 composite nanoparticles as additivities were reported. The ZrO_2/SiO_2 composite nanoparticles were synthesized and in situ modified with aluminum zirconium coupling agent. Such composite nanoparticles dispersed homogenously in lubricating oil with good stability. The Zeta potential value indicated that static repellency of modified ZrO_2/SiO_2 becomes stronger than that of the as-prepared nanoparticles. The modified ZrO_2/SiO_2 nanoparticles were well dispersed in lubricating oil that was still transparent after 72 h. Therefore, the ZrO_2/SiO_2 composite nanoparticles changed from hydrophilic to hydrophobic after the surface modification. Lubrication properties of such nano-oil were investigated with four-ball friction and wear experiments. It was found that the optimized concentration of the modified ZrO_2/SiO_2 composite nanoparticles was 0.1 wt% and the averaged reduction of friction coefficient was 16.24%. In this case, the wear scar diameter of the vertical was reduced by 14.59%. Moreover, the negative wear and tear was observed in thrust ring friction and wear tests when the concentration was 0.1 wt% due to the dynamic self-healing deposition effect of the nanoparticles. It was expected that the frictional heat was reduced and viscosity was increased. Therefore, the oil film was preserved at high load and the lubricating properties were enhanced.

Acknowledgments The authors acknowledge the financial support from National Science Foundation of China (50572034). B. Cai is an Oversea Taishan Scholar and thank the financial support from UJN for a new faculty.

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