Research Article

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Tribological performance of nano-diamond composites-dispersed lubricants on commercial cylinder liner mating with CrN piston ring

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Abstract: This work investigated the effect of nanodiamond (ND) additives on the tribological properties of CrN-coated piston ring mating with the chromium-plated and BP alloy iron cylinder liners, which is one of the key friction pairs in the internal combustion engines. To enhance the dispersion of the NDs in the base oil, the surface of ND particles was modified with polyaniline via in situ polymerization. The friction and wear as well as the scuffing characteristics of the friction pair lubricated with different contents of ND composite-added base oil were evaluated by using the reciprocating tribotests, which are close to the actual conditions. The wear surface morphologies and elements distribution were analyzed to explore the wear behaviors and the associated mechanisms of friction pairs under the lubrication incorporated with the ND composites. The results show that the ND additive is beneficial for the pair of Cr liner and CrN-coated piston ring in the friction and wear as well as scuffing properties, and the best concentration of ND additive is expected to be around 1 wt%. But for the BP liner, the developed nanocomposite has a negative impact. The friction force and the wear loss of the pair

Keywords: cylinder liner/piston ring, nano-diamond composite additive, polyaniline, tribology performance, scuffing properties

1 Introduction

The reduction in fuel consumption in modern vehicles is the main driving force for new innovations in technologies [1,2]. One main strategy is to develop the lightweight materials to achieve better fuel efficiency [3-7]. Decreasing the friction losses of the friction pairs in engines is considered as a promising direction as well [8,9]. The cylinder liner and piston ring (CPR) is one of the most crucial friction pairs in the internal combustion engine, and the lubrication and friction properties of CPR affects the fuel efficiency, system durability and even the life of the internal combustion engine directly. When the internal combustion engine moves toward high-power density and low fuel consumption, the engine pressure, and the temperature increase significantly, which leads to a worse condition for CPR. As a result, the faster degradation and the higher frictional work loss of the friction pair substantively affect the performance of the whole engine. Thus, improving the friction performance and prolonging the service life of CPR are of vital significances in the development of the modern internal combustion engines [10-12].

One of the most effective ways to improve the tribological performance of the CPR is by seeking the high-quality and high-efficiency engine oils, which play a key role in lubrication and cooling of engine components [13–15]. Usually, the high-performance lubricating oils consist of the base oil and a number of specific additives. The traditional additives such as viscosity index improver, antioxidants, friction modifiers, and extreme pressure

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lubricated by the ND composite-added oil are even worse than that tested with the base lubricating oil.

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antiwear agent promote the lubrication property of the base oil dramatically. However, most of the additives used in the internal combustion engine oil contain sulfur, phosphorus, chlorine, and other environment-unfriendly elements, which will cause environmental pollution [16–19]. Nowadays, with the continuous development of nanotechnology and nanomaterials, the researchers put effort into adding nanomaterials in lubrication oil to exploring the lubricants that deliver excellent performance [18–20]. A series of studies have indicated that the nanoparticles as lubricant additives can improve the tribological behavior of lubricants significantly because of their unique physical and rheological properties [21–24]. In addition, nanolubricants have more excellent antiwear and antifriction effects than some finished lubricants [25,26].

Among many nanoadditives, nanodiamond (ND) has attracted much attention because of its stable chemical properties, spherical shape, and high hardness [27–31]. Most of the studies on the lubrication property of ND-added base oil/commercial oil were performed with the traditional wear tests, such as block-on-ring [32], ball-on-ring [33], and pin-to-disc [34], and carbon steel was the commonly used friction pair material. Their results found that the ND particles can improve the tribological performance. To validate the applicability of the NDs in the engine oil, the experiment condition needs to be close to the actual conditions, and the friction pair should be collected from the real engine parts. Moreover, the scuffing is a vital problem that strongly affects the reliability and the lifespan of the engine [35-38]. However, fewer studies have focused on the effect of NDs on the antiscuffing performance; thus, the associated mechanisms are still not well understood.

This work aims to determine the effect of ND additives on the friction reduction and antiwear as well

as scuffing properties of the CPR system. The actual CrN-coated piston ring and chromium-plated cylinder liner (Cr liner)/boron-phosphorus alloy cast iron cylinder liner (BP liner) were selected. The stepwise load wear and starved oil-based scuffing tests were conducted with the in-house tribo device, which was developed for the CPR. The wear surface morphology and element distribution were analyzed to explore the influencing mechanism of the ND additives on the tribological performance of the cylinder liner-piston ring friction pair.

2 Experimental details

2.1 Nanoparticles and lubricating oils

The base lubricant used in this study was commercially available synthetic oil (HVI-5 base oil). The ND powder was purchased from Nanjing XFNANO Materials Tech. The average size of the ND particle ranges from 5 to 10 nm. This study used polyaniline as the surface modifier, which contributes to the stabilization of ND dispersed in the base oil. The polyaniline (PANi)modified ND particles were prepared with an in situ polymerization method, according to our previous work [39]. Figure 1(a) shows the SEM image of the polyaniline-modified ND particle. ND maintains uniform spherical particle morphology after the surface modification. From the XRD result (Figure 1(b)), the characteristic peaks of PANi at $2\theta = 9.5$, 15.9, 20.1, and 25.5° could all be observed, which reveals the successful synthesis of polyaniline-modified layer. On the other hand, the peak

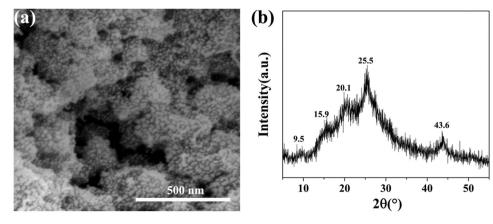


Figure 1: (a) SEM image and (b) XRD pattern of the polyaniline-modified ND particle.

at $2\theta = 43.6^{\circ}$ is corresponding to the (111) plane of ND, which shows the good preservation of ND. The surface-modified nanoparticles were then predispersed by a combination of mechanical stirring and ultrasound irradiation in a reference oil. Then, this preconcentrate ND composite was diluted in the partially formulated base oil to obtain the nanolubricant. The concentration of nanoparticles was investigated included 0.5 wt%, 1 wt%, 2 wt%, and 3 wt%.

2.2 Friction pairs

The developed lubricant with the ND additive was implanted in the typical friction pair of cylinder liner and piston ring, and the tribological performance of the pair directly indicates the effectiveness of the ND-based lubricant oil. The CrN-coated piston ring provided by CYPR ASIMCO Shuang Huan Piston Ring CO., Ltd was selected as the test specimen. The thickness of the CrN coating is about 30 µm, and the hardness is 1,066 HV_{0.1}. Cr liner treated by a platform honing process was selected as the counterpart materials, whose inner and outer diameters of the liner are 110 mm and 126 mm. The surface roughness of Cr liner is $0.8 \,\mu m$ (R_a), and the hardness is 701 HV_{0.1}. BP liner was applied as the other counterpart specimen, which consists of lamellar pearlite, graphite, and a small amount of phosphorus eutectic. The surface roughness of BP cylinder liner is $0.4 \, \mu m \, (R_a)$, and the hardness is $170 \, \text{HV}_{0.1}$. The two liners were cut into 40equal portions along the circumference (the central angle of the actual liner is about 9°, the arc length is 10 mm, and the length of cylinder liner specimen is 44 mm) [40].

2.3 Tribological test

The stepwise load tests and scuffing resistance tests were used by using the reciprocating sliding tribotester, which is purposely designed to simulate the working conditions of the actual top piston ring and cylinder liner [41]. Stepwise load tests adopt the way that the load increases with per 40 min, and the whole test was supplied with adequate lubricating oil at the speed of 0.1 ml/min. Before loading, the running-in stability under the previous load must be guaranteed. In other words, the friction coefficient must be kept at a stable value. The scuffing resistance tests were conducted with the reciprocating sliding tribotester as well, and it was divided into two stages: the running stage (included the light load period and higher load period, and the speed of lubricating oil is 0.1 ml/min) and the oil starvation stage. The lubricating oil supply was cut after a running stage, then the time interval between the oil cutoff and the onset of the scuffing (friction force increases sharply) was recorded to represent the scuffing resistance capacity [36]. At least five tests for each friction pair were conducted under the same conditions (Table 1).

The wear depth measured by the Olympus LEXT OLS4000 confocal laser scanning microscopy (CLSM) was used to characterize the wear loss of the liner and piston ring specimens. Before and after each stepwise load test, the surface morphologies and chemical composition of cylinder liner specimens and piston ring specimens were examined by ZEISS-SUPRA 55 SAPPHIRE scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS).

3 Results and discussion

3.1 Effect of ND additives on the friction performance of CrN-coated ring mating with different cylinder liners

Figure 2 shows the friction force of Cr liner/CrN-coated piston ring changing with different ND concentrations in the stepwise load tests. It can be seen from the variation trend of friction force that the ND additive has a remarkable effect on the tribological performance of base oil between Cr liner and CrN coating piston ring.

Table 1: Experimental conditions of the stepwise load tests and scuffing resistance tests

Experiment	Parameters of experiments 200 rpm 150°C 10–40 MPa (begin from 10 MPa, then load 10 MPa per 40 min)	
Stepwise load test Scuffing resistance tests		
	Running-in stage	120°C 10 MPa 10 min, 190°C 20 MPa 150 min
	Starvation stage	Oil cut until occur scuffing

Besides raw base oil (black line), the friction force obtained from the tests lubricated with the ND composite added oil is relatively stable and lower (red, blue, green, and purple lines). Under the condition of the base oil without ND particles, the friction force begins to fluctuate, and scuffing occurs when the load increases to 30 MPa. In the meanwhile, when the load increases to 40 MPa, the friction force increases sharply, and the surface of the friction pair is severely scratched.

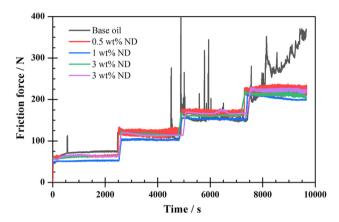


Figure 2: Variation of the friction force between Cr liner and CrN piston ring.

By comparing the friction coefficients between these five friction pairs lubricated by base oil with different concentrations of ND particles, the friction coefficients of the friction pairs with the ND lubrication oil were all smaller than that of the base oil regardless of the concentration of ND (see Figure 3). Meanwhile, the friction coefficients decrease first and then stabilize with the load increase under the ND lubrication oil. Although the friction coefficient of the tribopair under base oil decreases with the increase of load (from 10 to 20 MPa), it is still higher than the friction pairs lubricated by ND lubricating oil. With the respect of friction reduction, the best amount of ND added in the base oil is expected to be around 1 wt%.

The friction force of the BP liner and the CrN-coated piston ring changing with different ND contents in the stepwise load tests is illustrated in Figure 4. Contrary to the change of the friction force in the Cr liner/CrN-coated piston ring, ND lubrication seems to have no effect on improving the tribological properties. Furthermore, the friction force between tribopairs with the ND dispersed oil is all even higher than that obtained with the base oil and exhibits extreme instability. In addition, the ND-lubricated tribopairs needs a longer running-in time to reach a relatively stable state after each load

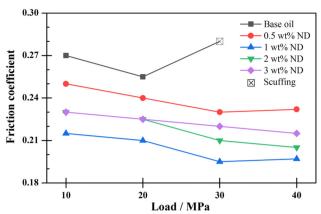


Figure 3: Variation of the friction coefficient between the Cr liner and the CrN-coated piston ring.

increase, and the scuffing trends to occur at the high load, while the base oil is comparatively stable and the friction force is basically lower (see the black line).

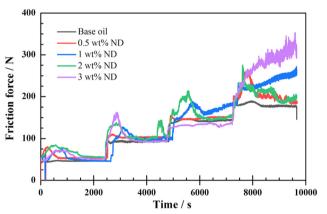


Figure 4: Variation of friction force between the BP liner and the CrN-coated piston ring.

Figure 5 exhibits the friction coefficients of the BP liner/ CrN-coated piston ring in stepwise load tests. As can be observed, the friction coefficient under the base oil is the lowest among all the tribopairs in different loads, and it first increases and then decreases with the increase of load (from 10 to 40 MPa). Meanwhile, the friction coefficients between other four tribopairs under ND lubrication exhibits unstable and are all higher than the friction coefficient under base oil. In addition, other four tribopairs under the condition of ND lubrication exhibit unstable friction force under higher load (20 or 30 MPa), implying the developed nanoadditive suppresses the lubrication of the base oil for the BP liner matching with the CrN-coated ring. It should be noted that the wear depths of the tribopair are not provided, because the wear behavior changes due to the onset of scuffing, and the material loss caused by the abnormal wear shows no indicative value.

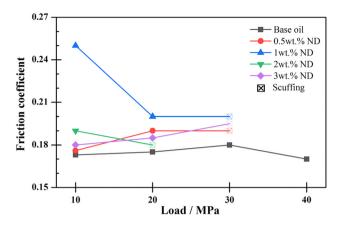


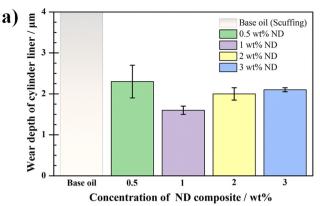
Figure 5: Variation of the friction coefficient between the BP liner and the CrN-coated piston ring.

3.2 Effect of ND additives on the wear performance of CrN-coated ring mating with different cylinder liners

3.2.1 Effect of ND additives on the wear performance of Cr liner and CrN-coated ring pair

Figure 6 shows the wear depth of the cylinder liner and piston ring specimens with different concentrations of ND additive. In addition to the occurrence of scuffing between the tribopairs under the base oil condition, the wear depth between the other four tribopairs under ND lubrication can be effectively reduced. The wear depth of both the Cr liner and CrN-coated piston ring first drops and then rises with the increase of the ND content (from 0.5 wt% to 3 wt%). At the optimal ND concentration of 1 wt%, the lowest wear depth is obtained. The base oiladded ND additive exhibits the relatively lower wear depth, indicating the better wear resistance. It can thus be concluded that the ND modified with PANi as an additive in the base oil between Cr liner/CrN-coated piston ring friction pair has good antiwear and friction reduction properties, which are much better than that of the base oil without any additives under the same conditions, and the optimal additive concentration is around 1 wt%.

The worn micrographs of the friction pair are shown in Figure 7. Severe plastic deformation and furrow could be found on the Cr liner surface lubricated with the base oil (Figure 7(a); ND% = 0%), whereas the plastic deformation and furrow on the worn surface lubricated with the base oil containing ND particles are significantly inhibited (Figure 7(a); ND% = 0.5-3%). When the concentration of ND is 1 wt%, the cross-hatch honing pattern is preserved very well. With the further increase



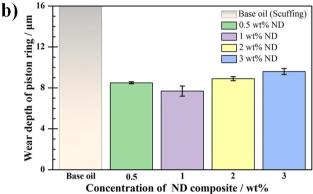


Figure 6: The wear loss of the friction pair: (a) wear depth of the cylinder specimen and (b) weight loss of the liner specimen.

in the ND composite content, the honing grooves gradually almost worn away (see Figure 7(a); ND% = 3%). Regarding the worn surface of the CrN-coated piston ring (Figure 7(b)), the degree of wear shows the similarity with that observed in the liner. With the ND composite lubricants, the wear grooves and scars are noticeably fewer and narrower than those found in the ring surface lubricated by the base oil. Moreover, the most slightly wear surface is observed in the 1 wt% lubrication. Consequently, adding the ND composite in the base oil can remarkably improve the wear resistance of Cr liner mating with the CrN-coated piston ring.

A reasonable explanation for the antiwear mechanism of ND particles is possible that the repairing effects (ND composites filled in the micro pits on the friction pair surfaces results in a smoother surface) [42–44]. The typical SEM morphology and EDX results of the wear surface of Cr liner when the concentration of ND composite additive is 1 wt% are illustrated in Figure 8. Only the Cr and O elements can be found on the plateaus of the Cr liner surface (Figure 8(a)). Cr is the dominating matrix element of Cr-plated coating, and O might originate from oxidation during sliding. However, more black sediments are deposited in the surface pit after the test.

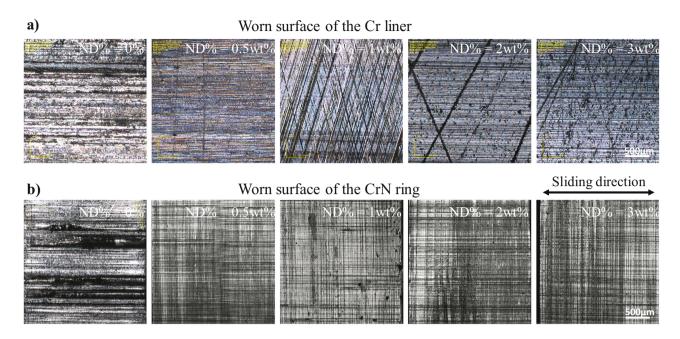


Figure 7: Worn micrographs of the Cr liner (a) and its counterpart CrN piston ring (b) lubricated with different ND content lubricants.

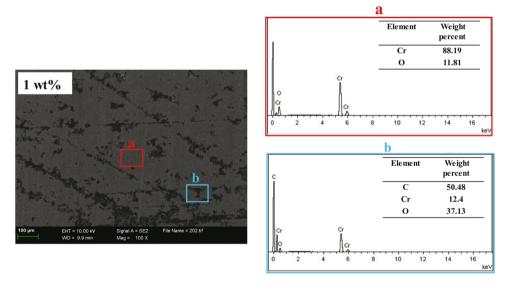


Figure 8: SEM micrographs and EDX spectra of Cr liner specimens after test (a) flat zone and (b) defect zone.

The elemental analysis of black sediments reveals that the main element of black sediments is C (Figure 8(b)). It is well known that C element can be resulted from the carbon deposition due to the combustion of furl or lubricating oil, but it has been reported that the occurrence of carbon deposition needs a temperature higher than 300°C [45]. As the test was performed at the temperature of 150°C, it is considered that the observed black sediments mainly come from the ND composite. The ND composites are deposited in the pits during

sliding, resulting in a smoother surface and contributing to sustain the oil film. Thus, the friction and wear of the friction pair can be reduced [46].

The surface roughness of Cr liner specimens before and after wear test is shown in Figure 9. It can be seen that the roughness in both the middle stroke and dead center decreases compared with the base oil lubrication surface, indicating the surface polishing effect of the ND composite. Furthermore, the roughness near the dead center is lower than that near the middle stroke, and this

is because the friction force of the dead center is larger than that at the middle stroke in each reciprocation cycle [36]. Thus, the polish process is more effective. On the other hand, the lowest surface roughness is observed under the optimum concentration of ND composite (ND% = 1 wt%), and the smoother surface is more conducive to the formation of lubricating oil film. The ball-bearing effect of the ND particles may be activated as well [27]; therefore, the low friction and wear loss, as well as the slightly worn surface of the friction pair, was obtained. Noted that the amount of nanoparticles is not the more the better. The agglomeration will occur if the ND particle is over-added in the lubrication oil, thus, the abrasive dust can be formed between the friction pairs. As a result, the surface roughness increases again due to the abrasive wear (Figure 7; ND% = 2%, 3%).

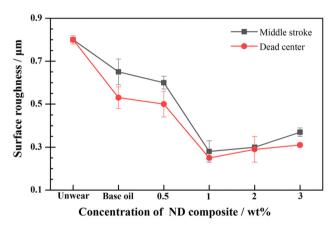


Figure 9: Surface roughness of the Cr liner before and after the test.

3.2.2 Wear micrographs and elemental analysis of BP liner/CrN ring after stepwise load tests

Figure 10 presents the wear micrographs of the BP liner and the CrN-coated piston ring after stepwise load tests. Under the condition of the base oil, abrasion along sliding direction exists on the surface of the BP liner and piston ring after tests although the honing marks on the surface of liner are somewhat visible as shown in Figure 10(a) (ND% = 0-3%). Compared with the base oil, the scratches on the BP liner sliding against the CrN-coated piston ring are more apparent under the ND composite-added lubrication. Figure 10(a) (ND% = 2%, 3%) presents the wear damages on the BP liner surface. The results correspond to the high and unstable friction force. For the CrN surface, the severe wear can be observed as well.

Figure 11 presents the wear surface of the BP liner under the ND composite-added lubrication. Similar to the phenomenon found in the pair of the Cr liner and CrN coating, many black sediments were deposited on the surface pits after the test. Through the EDS spectrum, black sediments are also dominated by the C element. As the hardness of the BP liner is very low, it is considered that the hard NDs are pressed into the soft surface of the BP liner during relative sliding of tribopairs, and the surface damage caused by ND particles is aggravated with the continuation of relative sliding [47]. Consequently, the ND composites deteriorate the friction and wear properties of the BP liner and CrN-coated friction pair. According to the result, it can be inferred that ND additives will aggravate the wear rather than protecting the friction pair surface if the friction coupling surfaces are too soft.

3.3 Effect of ND additives on the scuffing resistance performance of base oil

Since the developed ND composite has no beneficial effect on the tribology performance for the BP liner, the influence of ND particles on the antiscuffing properties of the base oil was only explored for the friction pair of the Cr liner and the CrN-coated piston ring. Figure 12 shows the typical friction forces of the whole scuffing resistance tests with different lubricants subjected to a load of 20 MPa. As the lubricating oil is cut off after the running-in stage, the oil film can be hardly uniformly dispersed on the contacting surface [48]. Under such oil starved condition, the additives and the oil retention capacity of the friction pair determine the anti-scuffing performance. All the friction force variations show the similarity in trend, but the scuffing time of the ND composites lubricated friction pairs is considerably longer than that of the base oil condition, and 1 wt% ND composite content still exhibits the best scuffing resistance.

4 Conclusions

The surface of ND particles was covered with polyaniline by the *in situ* polymerization process, and the developed nanocomposites were then uniformly dispersed in the base lubrication oil as the antifriction additive. The stepwise load tests were conducted between the BP liner/Cr liner and CrN-coated piston ring specimens lubricated by the base oil with different nanocomposite contents. The effect of the ND additives on the friction

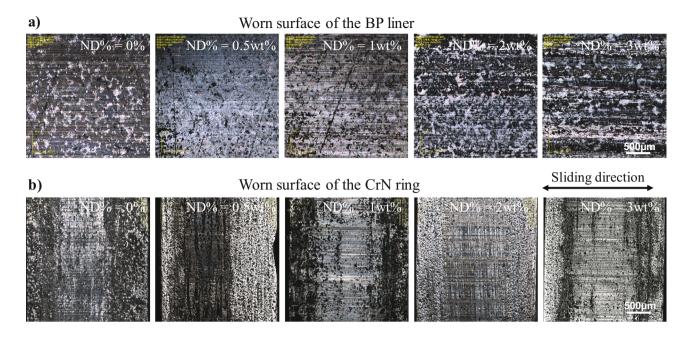


Figure 10: Worn micrographs of the BP liner (a) and its counterpart CrN piston ring (b) lubricated with different ND content lubricants.

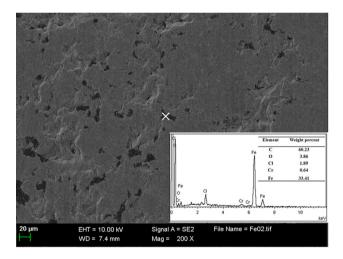


Figure 11: SEM micrographs and EDX spectra of cylinder liner specimens after test.

reduction and anti-wear as well as the scuffing properties were investigated, and the associated mechanisms were analyzed. The conclusions were drawn as follows:

- The ND additive is beneficial for the pair of Cr liner and CrN-coated piston ring in the friction and wear as well as scuffing properties, and the best concentration of ND additive is expected to be around 1 wt%.
- Regarding the BP liner and the CrN piston ring friction pair, the developed nanocomposite has a negative impact on the overall tribological performance. The friction force and wear loss of the pair lubricated by

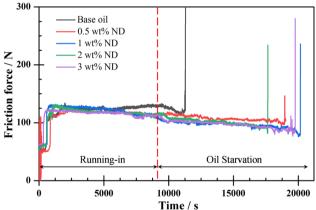


Figure 12: The typical friction force variation of the Cr liner and the CrN-coated piston ring under 20 MPa in scuffing resistance tests.

the ND composite-added oil are even worse than that tested with the base lubricating oil.

• The improved tribological performance is very likely resulted from the surface polishing and repairing effects of the nanocomposite. These effects can make the surface smoother. Smooth surface not only promotes more uniform distribution of the lubrication oil film but also avoids local oil film collapse, improving the bearing capacity of the lubrication oil film. However, over-added ND nanoparticles will cause the agglomeration, and even the abrasive wear, which strongly affects the tribological performance.

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