The Influence of Nanocomposite Carbon additive on Tribological Behavior of Cylinder Liner/Piston Ring

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Abstract. Nanocomposite Carbon additive were dispersed at varying concentrations (1, 3, 5wt%) in SN/GF-5 lubricants for automotive engines. Raman spectroscopy is used to characterize the morphology of carbon. The effect of Nanocomposite Carbon additive on the friction and wear properties of the piston ring friction pair is investigated by using UMT friction tester. The tribological mechanism of Nanocomposite Carbon additive is further investigated by scanning electron microscopy, energy dispersive spectrometer and three-dimensional shape spectrometer. The results show that Nanocomposite Carbon additive exhibits excellent antifriction performance at high load and friction coefficient at low load. The effect of the nanocomposite carbon additive is the best when the mass fraction is 3%; however, the nanocomposite carbon additive concentrations is too high, which will lead to increased wear under high load. The nanocomposite carbon particles can smooth the micro-convex of the friction pair surface and reduce the surface roughness. The contact area of the friction pair is significantly increased, and the pressure is significantly reduced. The nano-composite carbon avoids the breakage of the bearing oil film when the metal surface peaks contact each other, ensuring the integrity of the oil film and uniformly carrying a large load. The nanocomposite carbon lubricant additive shown in this study can reduce energy consumption and extend engine life, resulting in significant cost savings.

1. Introduction

Reduction in friction and wear is one of the most important objectives of tribological research [1]. With the rise of nanotechnology, many studies have been conducted in recent years using carbon nanomaterials as additive in lubricating oil to improve the tribological properties of lubricants. There are few commercial additive containing carbon nanomaterials, mainly because the dispersion and stability of nanoparticles in lubricants are not well solved [2]. The extremely fine grains of the nanoparticles, which have a large surface energy. Large self-aggregation tendency between particles, which form large aggregates after a period of time [3]. Nanocomposite carbon additive mainly contains Ultra-dispersed diamond graphite powder manufactured from explosives, which will not cause chemical pollution. Russia's Yu. Neverovskaya has successfully modified the surface of diamond with a coupling agent to improve the lipophilicity of the diamond and the suspension in the organic phase, which proposed a dispersion model for surface modification of diamond with silane coupling agent[4-5]. Red'kin et al. added a composite additive containing nanodiamond-graphite to the engine oil, and the antifriction and antitrust properties were significantly improved [6]. At the same time, the contents of elements such as sulfur, chlorine, phosphorus, and fluorine are lowered. The friction
coefficient is lowered, the smoothness of the friction pair is increased, and the noise is lowered [7]. After mechanochemical modification of nanocomposite carbon it can form a stable colloidal system in various lubricating oils and it can fill the micro-cracks and unevenness on the metal surface freely grind the sharp protrusion on the friction pair surface and remove the uneven peak of the friction pair. The addition of nanocomposite carbon additive to the lubricating oil can improve the working life of the engine and transmission and it can reduce surface wear [8]. The authors used the umt tester to carry out the reciprocating friction and wear test. The effects of tribological properties of nanocomposite carbon additives on cylinder liner piston rings were investigated. The morphology and EDS analysis of the wear scar of the cylinder liner were used to explore the Nanocomposite Carbon. The tribological mechanism of Nanocomposite Carbon additive under the frictional pair of cylinder liner/piston ring is discussed.

2. Experimental section

2.1. Materials

Ultra-dispersed diamond graphite powder was purchased from Nanjing XFNANO Materials Tech Co., Ltd. SN/GF-5 lubricant were provided by Tianjin Co., Ltd. T-161A High Molecular Weight Polyisobutylene Succinimide was supplied by Jinzhou Runda Chemical Co., Ltd. T-109 calcium alkyl salicylate was purchased from Xinxiang Richful Lube Additive Co., Ltd. Coupling agent of organic titanate were provided by Dalian Richon Chem Co., Ltd. Nanocomposite Carbon Lubricant fluid Density (15 °C) and Viscosity (40 °C) are 1.00 g/cm³ and 79.15 Cst. Ultra-dispersed diamond graphite nanoparticle size is 4nm. The upper and lower friction pair properties are 6×17×10mm, 45×34×8mm, \( R_a = 0.43 \mu m \) and hardness:55 HRC.

2.2. Characterizations and measurements

2.2.1. Configuring nano-composite carbon lubricant additive. Ultra-dispersed diamond graphite powder is mechanically chemically modified by a ball milling method to remove hard agglomeration of the nanoparticles. The nanomaterial is wrapped with a titanate coupling agent. The surface agglomerates are agglomerated by mechanical stress and activated to modify the surface crystal structure and physicochemical structure. The nanoparticle lattice undergoes displacement and internal energy increases. Under the action of external force, the titanate coupling agent acts as a surfactant to participate in the reaction and achieve the purpose of surface modification. The surfactant is coated with the surface of the particle by chemically adsorbing or chemically reacting the surface-active organic functional group with the surface layer of the nanoparticle. Nanocomposite Carbon additive with good lipophilic dispersion properties was prepared. The treated Nanocomposite Carbon additive was added to the SN/GF-5 lubricating oil, and the detergent T-109 and the dispersing agent T-161A were added. Different proportions of 1%, 3% and 5% Nanocomposite Carbon lubricant additive were prepared.

2.2.2. Tribotest rig description. The upper and lower specimens are obtained from the engine piston ring and the cylinder liner, and the dimensions are as shown in the table1. The main structural features of the test rig are shown in Fig. 1. The oil sample was dripped 1 ml before the test. The test was divided into a 30 s run-in and a 30-minute test phase. The run and phase load was 50 N. The test phase loads were 50, 100, 250 and 400 N, respectively, with a temperature of 100 °C, a stroke of 1 mm and a frequency of 10 Hz. The cylinder liner was placed in petroleum ether before and after the test and ultrasonically cleaned. The weight loss percentage of the liner is measured on the balance. Then, the three-dimensional surface topography instrument was used to observe the wear profile of the liner. Scanning electron microscopy and energy spectrometer were used to observe the wear profile of the liner and analyze the surface element composition of the wear scar.
3. Results and Discussion

3.1. Raman spectroscopy

Raman spectroscopy is a means of studying carbon structure efficiently and can characterize the morphology of carbon. The Raman spectroscopy of the Nanocomposite Carbon additive are shown in Fig. 2. As can be seen from the Fig.2, the broad Raman peak near 1329 cm\(^{-1}\) is the characteristic peak of the sp\(^3\) structure nano-diamond, and the Raman peak observed near 1580 cm\(^{-1}\) is the sp\(^2\) structure nano-graphite. Since the Raman scattering cross section of diamond is 1/60 of graphite, this indicates that nano-composite carbon has both nano-diamond and sp\(^2\) structure nano-graphite residue [9-10].

![Figure 1: Photograph of sample holders in UMT](image)

![Figure 2: Raman spectra of Nanocomposite Carbon](image)

3.2. Effect of Nanocomposite Carbon additive Content on Friction and Wear Properties of Cylinder/Piston Ring Friction Pairs

Fig. 3 shows the friction coefficient curve of a SN/GF-5 engine oil using a nanocomposite carbon additive with different mass fractions for the cylinder liner piston ring friction pair. It is found through the friction curve that the addition of nanocomposite carbon additive reduces the friction coefficient. When the mass fraction of the nanocomposite carbon additive is 3%, the friction coefficient is the lowest. The friction coefficient of the friction pair decreases first and then increases with the increase of the nanocomposite carbon mass fraction. The excellent antifriction and anti-wear properties of nanocomposite carbon are demonstrated [11]. It can be seen from Fig. 4 that the wear percentage of the nanocomposite carbon mass fraction of 3% is the lowest. The nanodiamond in the nanocomposite carbon can micro-cut the micro-protrusion of the worn surface. Therefore, the metal surface is smoother and the coefficient of friction is low. Excessive mass fraction of nanocomposite carbon will increase wear and tear.

![Figure 3: Coefficient of friction curves](image)

![Figure 4: The percentage of the friction pair mass loss](image)

3.3. Effect of load on friction and wear properties of cylinder/piston ring friction pair
Fig. 5 shows the average friction coefficient of the cylinder/piston ring friction pair using different mass fractions (0%, 1%, 3%, and 5%) of nanocomposite carbon additive engine oils at different loads (50N, 100N, 250N, and 400N). At low load (50N, 100N), the contact area of the friction pair is small. The oil film is discontinuous, and the effect of the nanocomposite carbon additive is not prominent. As the load increases, the contact area of the friction pair increases, and the nanoparticles in the nanocomposite carbon additive adsorb on the contact surface to improve contact. And it can enhance the carrying capacity of the oil film. At high loads (250N, 400N), the average coefficient of friction is lowest when the mass fraction of nanocomposite carbon is 3%. Figure 6 shows the cylinder/piston ring friction wear rate of different mass fraction nanocomposite carbon engine oils under different loads. With the increasing of the load, the wear rate of the cylinder/piston ring friction pair is increased. The wear rate of the friction pair using nanocomposite carbon mass fraction 5% engine oil is the highest.

3.4. Analysis of friction and wear mechanism

Fig. 7 shows the SEM and 3D morphology analysis of the wear scar at the 400 N Nanocomposite Carbon mass fraction of 0%, 1%, 3%, and 5% after the test. It can be seen from Fig. 7(a) that when the Nanocomposite Carbon additive with a mass fraction of 5% is added, the Nanocomposite Carbon in the contact zone of the piston ring of the cylinder liner increases the friction and wear, and a large number of pits and furrows appear, and the surface is uneven. The degree of wear is mainly due to abrasive wear. When there is no Nanocomposite Carbon additive in the contact zone of the cylinder/piston ring friction pair, the furrow still appears, which may be caused by the scratching of the cylinder liner in Fig. 7(b). It can be seen from Fig. 7(c) that when the mass fraction is 3%, Nanocomposite Carbon is added. After, furrows appear in the wear scar zone of the cylinder liner. The furrows are distributed throughout the wear scar zone, but the furrows are arranged neatly, the surface is smooth, and the cracks are significantly reduced. It can be seen from Fig. 7(d) that the cylinder liner wears is reduced. The surface is flat and the depth of the wear scar is shallow. In summary, the addition of an appropriate amount of Nanocomposite Carbon additive to the SN/GF-5 engine oil will greatly reduce the wear of the cylinder liner. Under different loads, the cylinder liner wear table is more distinct. Specifically, with the increase of load, the flatness of the wear surface decreases, and the depth of the furrow increases.

The 3D morphology of the wear surface of different concentrations of nanocomposite carbon lubricant after the friction and wear test is shown in Fig. 8. The three-dimensional topography mainly represents the distance between the peaks and valleys of the surface contour. In Fig. 8a, the three-dimensional topography of the mass fraction of nanocomposite carbon is 3%, and the distance between the peak and the valley is 3.49 μm. As the concentration of the additive increases, the depth of the wear scar increases significantly. Furrows and pits can be found on the worn surface. The maximum sample size of 5% is 12.07 μm (Fig. 8b).

The EDS analysis was performed on the region shown by the SEM in Table 1, and black cracks were found in the SEM image. The flake graphite confirmed as a matrix by spectrum 1.2. When 1%
and 3% Nanocomposite Carbon were added to SN/GF-5, the wear surface element composition was Fe, C, Mn, Si and other matrix elements, indicating that no other elements on the friction pair surface participated in the friction reduction. When the mass fraction of Nanocomposite Carbon in SN/GF-5 is 3%, the content of C, Mn, Si and other elements on the wear surface decreases (spectrum 3.4.). It is indicated that the addition of the Nanocomposite Carbon additive forms a reaction film [12].

![Figure. 7 SEM photograph of cylinder liner worn surfaces for (a) 5% (b) 0%, (c) 3% and (d) 1%](image)

**Table 1.** EDS spectra and elemental analysis of cylinder liner worn surfaces

| Spectrum | Element mass fraction /% |
|----------|--------------------------|
|          | Fe  | C     | O    | Si   | Mn   | F    |
| 1        | 0.63 | 98.29 | 1.08 | 0    | 0    | 0    |
| 2        | 0    | 99.01 | 0.91 | 0    | 0    | 0    |
| 3        | 89.89 | 6.66  | 0    | 1.44 | 0    | 2.01 |
| 4        | 88.49 | 6.91  | 0    | 1.10 | 1.50 | 2.00 |

**4. Conclusions**

a. At low load (50N, 100N), the anti-friction effect of the nanocomposite carbon additive on the cylinder/piston ring friction pair is not obvious. At high loads (250N, 400N), the nanocomposite carbon additive has a significant effect on the friction reduction of the cylinder/piston ring friction pair.

b. Excessive Nanocomposite Carbon additive will aggravate the wear of the liner/piston ring friction pair, and the wear form is mainly abrasive wear. The amount of wear of the liner increases to the increase in the mass fraction of Nanocomposite Carbon additive in the SN/GF-5 engine oil.

c. The addition of the nanocomposite carbon additive to the lubricating oil can enhance the bearing capacity of the lubricating oil film. The adsorption of nanoparticles in the nanocomposite carbon
will adhere to the metal surface to reduce wear. The micro-cutting action of the nano-diamond in the nanocomposite carbon enables the surface of the friction pair to be smoother.

**Figure. 8** 3D morphologies of cylinder liner worn surfaces for (a) 3% and (b) 5%

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