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Tribological and tribochemical properties of magnetite nanoflakes as additives in oil lubricants

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ABSTRACT

This detailed the tribological and tribochemical properties of magnetite (Fe_3O_4) nanoflakes used as additives in #40 base oil in a four-ball tribo-tester. The average friction coefficient of the friction pair for lubricant containing the Fe_3O_4 nanoflakes of 1.5 wt% as a lubricant additive in the base oil is decreased by 18.06% compared to that of solely base oil. The chemical composition of base oil with the Fe_3O_4 nanoflake additives did not change during the 48-h friction assessment. The decreased saturation magnetization and increased coercivity of magnetite nanoflakes occurred due to the distortion of the basal planes and the presence of hematite (α-Fe_2O_3) generated by the tribochemical reactions during the friction process. The multi-layer low-shear-stress tribochemical lubrication films on the surface of the friction pair could form because the nanoflake particles arrange and adhere onto the surface of the friction pair in an orderly manner, and the tribochemical reactions of the friction pair in the presence of the nanoflakes occur as $Fe \rightarrow FeO \rightarrow Fe_3O_4 \rightarrow \gamma$-$FeOOH \rightarrow \gamma$-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$. The formation of the films can improve the tribological properties.

1. Introduction

Nanoparticles have been used as lubricant additives in recent years (Cao, Zhang, An, & Wang, 2008; Padgurskas, Rukuiza, Prosyčevas, & Kreivaitis, 2013; Qiao & Xu, 2005; Wo, Hu, & Hu, 2004; Zhao, Bai, Fu, Zhao, & Yan, 2012). Recent work has shown that nanoparticles, particularly some nanoflakes such as MoS_2 (Wo et al., 2004), serpentine (Cao et al., 2008) and graphite (Qiao & Xu, 2005), may enhance friction performance more than the conventional solid lubricants. These nanoparticles can produce multilayer films with a lower shearing stress on the surface of friction pair, repairing scratches or craters and reducing the friction coefficient (Guo, Gu, & Xu, 2003; Huang, Tu, Gan, & Li, 2006; Li & Zhen, 2004). The possible tribochemical reactions of a friction system that involve the friction pair materials, lubrication media (i.e., oil and solid nanoparticles) and environmental atmosphere during the friction process are interesting. The tribochemical reactions that occur during the lubrication process may influence the performance of lubricating oil containing nanoparticles (Dong & Hu, 1998; Gao & Zhang, 2000; Hu & Dong, 1998; Hu et al., 2002; Willermet et al., 1995; Xue & Zhang, 2009). Willermet et al. (1995) studied the reaction of zinc dialkyl dithiophosphates (ZDDP) on a steel surface; the ZDDP friction film promoted anti-wear properties via the tribochemical effect. Xue and Zhang (2009) reported that TiO_2 nanoparticles deposited on the surface of a friction pair formed a thin ceramic film that combined with the friction pair or formed a tribochemical reaction film to reduce the friction and wear. Hu et al. (Dong & Hu, 1998; Hu & Dong, 1998; Hu et al., 2002) investigated the tribochemical effect of borate nanoparticles during the lubrication process; the borate first decomposed to B_2O_3 before tribochemically reacting with Fe to form FeB and FeB_2, producing anti-wear films with superior tribological performance. Therefore, investigating the tribochemical reactions and the structure or component changes of the participating parts in a friction system is important (Xue & Zhang, 2009). Some magnetic nanoparticles (i.e., Fe_3O_4) were used as lubricant additives instead of plastic solid nanoparticles (Hu, Dong, & Chen, 1998; Jiao, Hu, & Wang, 2011; Zhang et al., 2008). The magnetic nanoparticles used in lubricant oil, particularly nanoflake particles, may reduce the gravitational and centripetal forces, preventing leakage and pollution (Zhang et al., 2008) and imparting better lubrication efficiency and performance. Hu et al. (1998) reported that the Fe_3O_4 nanoparticles with irregular morphology could improve anti-wear performance as a lubricant additive. Jiao et al. (2011) also investigated the improvement of the anti-wear performance in a friction

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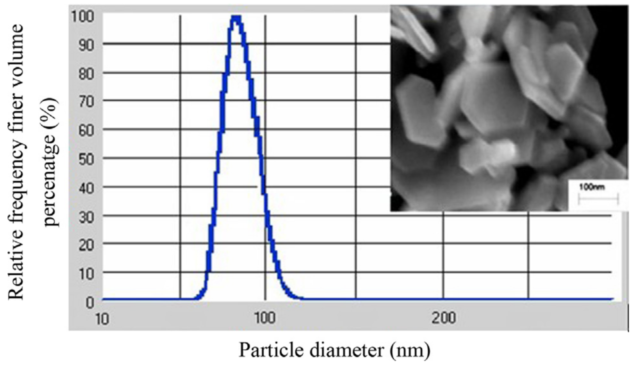

Fig. 1. Morphology and particle size distribution of the Fe_3O_4 nanoflakes (Hu & Wang, 2009).

system incorporating a small amount of Fe_3O_4 nanoparticle additives. These studies, however, have not yet addressed the possible tribochemical reactions in friction systems with magnetic nanoparticles.

This paper investigated the tribological and tribochemical properties of Fe_3O_4 nanoflakes as a solid lubricant additive in base oil using a four-ball tribo-tester. In addition, the friction and wear in friction pairs incorporating various concentrations of the nanoflakes were also analyzed.

2. Experimental

2.1. Materials

Hexagonal magnetite nanoflakes utilized were synthesized using a weak magnetic field-assisted oxidation-co-precipitation method that was described in our previous work (Hu & Wang, 2009). Fig. 1 shows the morphology and particle size distribution of the synthesized Fe_3O_4 nanoflakes. For the effective dispersion of Fe_3O_4 nanoflakes in the base oil, the surface of the Fe_3O_4 nanoflakes was coated and modified using oleic acid (Tianjin Kermel Chemical Reagent Co., Ltd., Tianjin, China) (Zhu, Song, Qiu, & Zhang, 2011). The Fe_3O_4 particles in lubricant oil adsorbed a massive amount of —OH that adsorbed H^+ ions in acidic environment, producing positively charged particles. Additionally, the homolysis of —C=O— occurred to produce two equal —C—O— single bonds that integrated with the Fe_3O_4 nanoflake surfaces due to the Coulomb force (Hong et al., 2006). In addition, the surface-modified nanoparticles in the oil were rigorously dispersed using a high-speed stirred bead mill (Sanxing Feirong Machine Co., Ltd., China) at 6000 rpm for 30 min (Xie, Rielly, Eagles, & Özcan-Taşkin, 2007) and an ultrasonic bath for 5 min to ensure that the nanoparticles were dispersed in the oil (Li et al., 2007). The resultant stable lubricating oils containing nanoflake particles at various concentrations were utilized for the experiments. The details regarding the effective dispersion and modification of Fe_3O_4 nanoflakes in lubricating oil was also provided in our previous work (Hu, Wang, & Pan, 2012). The mass percentages of nanoflake particles mixed with #40 base oil (Sinopec Co., Ltd., China) were 0.0, 0.5, 1.0, 1.5, and 2.0 wt%, respectively.

2.2. Equipment and procedure

The friction and wear performances were examined using a model MRS-10A four-ball tribo-tester (Jinan Jingcheng Jishu Co., Ltd., China) at 1450 rpm under a 392 N applied load for 0–48 h. The friction pairs used were GCr15 steel balls 12.7 mm in diameter with the hardness HRC59-61 and the following composition: 96.50–97.49% Fe, 0.95–1.05% C, 0.15–0.35% Si, 1.30–1.65% Cr, 0.20–0.40% Mn, ≤0.02% S, and ≤0.027% P. Before each test, the steel balls were cleaned with petroleum ether and dried. After the experiment was completed, the Fe_3O_4 nanoflakes were separated from the oil using magnetic and centrifugal separation methods, and the particles and friction pairs were cleaned in an ultrasonic bath with petroleum ether for 15 min.

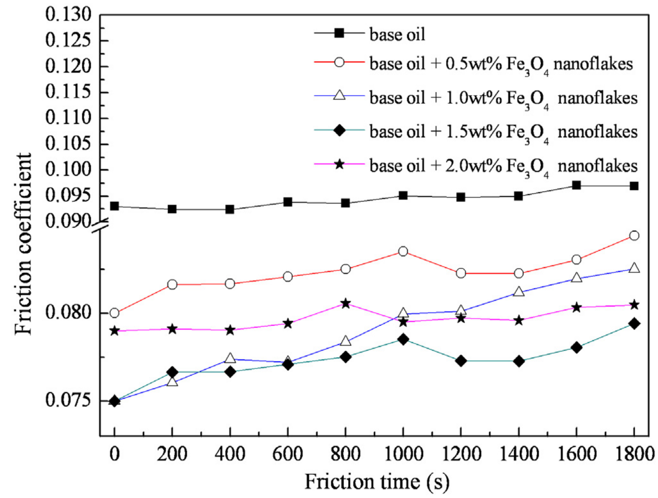

Fig. 2. Friction coefficients of the friction pair at various Fe_3O_4 nanoflake concentrations (392 N, 1450 rpm).

2.3. Characterization

The Fe_3O_4 nanoflakes were characterized with an X-ray diffractometer (XRD, Co target, Philips Co., Ltd., The Netherlands), an acoustic particle sizer (Matec Applied Sciences Co., Ltd., USA), a FlowSorb III Surface Area Analyzer (Micromeritics Co., Ltd., USA), a field emission scanning electron microscope (FESEM, JSM 6330F, JEOL, Carl-Zeiss Co., Ltd., Germany) and a vibrating sample magnetometer (VSM, Lake Shore Cryotronics Inc., USA). The base oil was analyzed with a Fourier transform infrared spectrometer (Bruker Optics Co., Ltd., Germany). The friction pair was characterized with a Laser Raman spectrometer (HORIBA Scientific Co., Ltd., Japan), an energy dispersive X-ray spectroscope (EDS, model INCA 250, Oxford Instruments Co., Ltd., UK), an X-ray photoelectron spectroscope (XPS, model Axis Ultra DLD, Kratos Co., Ltd., UK), a FESEM and an atomic force microscope (AFM, model MutiMode-III, Veeco Instruments Co., Ltd., USA). The wear scar diameter (WSD) of the friction pair was examined under a metallographic microscope at 100× magnification.

3. Results and discussion

3.1. Tribological properties

Fig. 2 shows the friction coefficients of the friction pair in #40 base oil with the surface-modified magnetite nanoflakes at various concentrations. Clearly, the friction coefficients with the magnetic nanoflakes were lower than those with only the #40 base oil. Additionally, the friction coefficients decreased when the nanoflake concentration increased, and the lowest friction coefficient was obtained at 1.5 wt%. Compared to the case with the original base oil, the friction coefficient for the oil with 1.5 wt% nanoflakes was decreased by 18.06%. Fig. 3 shows the WSD of the friction pair at various nanoflake concentrations. The WSD decreased before increasing as the concentration rose. The lowest WSD was obtained at 1.5 wt% nanoflakes; the WSD in this system decreased by 11.2%

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