Journal of Industrial and Engineering Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Reinforcing effect of Lewis acid–base interaction on the high-temperature colloidal stability and tribological performance of lubricating grease

Nan Xu[a,b], Weimin Li[a], Ming Zhang[a], Xiaobo Wang[a,b,*]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
[b] Qingdao Center of Resource Chemistry and New Materials, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Qingdao 266000, China

ARTICLE INFO

Article history:
Received 21 July 2016
Received in revised form 14 October 2016
Accepted 16 October 2016
Available online xxx

Keywords:
Tribological performance
Lewis acid–base interaction
High temperature
Lubricating grease
Colloidal stability

ABSTRACT

The high-temperature tribological performance of lithium grease is enhanced by addition of Lewis acid borate ester, which could interact with Lewis base RCO_2^- of lithium 12-hydroxystearate (LHS, constitute the thickener fiber network of lithium grease) to form a Lewis acid–base complex. Important details about the Lewis acid–base complex and its reinforcing effect on the tribological performance are elucidated by means of SRV oscillating friction and wear tester (SRV), Fourier transformation infrared spectroscopy (FTIR), TGA–DSC, and rheological methods. The experimental results strongly suggest that there is a Lewis base–acid interaction between the boron atom of borate ester or boric acid and the oxygen atom of RCO_2^-. Lewis acid centers can serve as second-level linking points to reinforce the strength of the thickener fiber network and further improve the colloidal stability of lubricating grease. Compared with pure LHS, the Lewis acid–base complex displays higher thermal stability, allowing lithium grease to be applied to higher temperature. Because of the enhancement of thermal stability and colloidal stability, film-forming property under high temperature can be greatly improved, resulting in >15% friction and >95% wear reductions.

Introduction

Friction and wear between lubricated bearing surfaces are unavoidable and are an important reason for the failure of mechanical components. To date, about 90% rolling bearings are lubricated with lubricating grease [1]. Unlike the oil lubrication, the contacts of grease-lubricated rolling bearing operate under starved condition for most application environments [2–4]. The film-forming property of lubricating grease is crucial to the service performance of rolling bearings especially for the startup and shutdown processes, which correspond to the mixed or boundary lubrications and are the major wear-emerging stage. It was estimated that over 40% of premature failures of rolling bearings are related to the lubrication [5]. In addition, the structural character and evolution behavior resulting from the former have a significant effect on the formation of lubricating film. It is therefore necessary to interpret the lubricating mechanisms of lubricating grease under mixed or boundary lubrication from the microstructure point.

Recently, it was reported that the film-forming property of lubricating grease was significantly influenced by the morphologies of the grease thickener fiber, especially for the low to medium speed range [6–9]. This is because lubricating grease tends to behave as Newtonian fluid under the high speed and the film thickness is mainly up to the physicochemical properties of base oil. With decreasing the speed, the character of non-Newtonian fluid of grease will gradually emerge and the effect of thickener fiber morphologies on the film-forming property become more prominent. Specifically, thickener fiber with smaller dimension benefits film-forming property under medium speed whereas large fiber dimension is more suitable for low speed. On basis of the previous work [10,11], the adaptability differences toward speed conditions can be ascribed to distinct structural characters, which can be elucidated via rheological methods [12–16]. We found that thickener fiber with larger dimension displayed higher structure strength but a lower response rate. While for the grease with smaller thickener fiber, a contrary trend was observed. More

* Corresponding author at: State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China.
E-mail addresses: wangxb@lzb.ac.cn, wangxb@licp.cas.cn (X. Wang).

http://dx.doi.org/10.1016/j.jiec.2016.10.026
1226-086X/

importantly, under high speed the effect of response rate on the tribological performance is superior to that of structure strength. However, the structure strength plays a crucial role in mixed or boundary condition due to its enhancement on the film-forming property, especially for the high temperature conditions.

In the previous works [17–19], borate ester, which acts as Lewis acid, has been suggested for enhancing the transference numbers of the lithium ions in the battery electrolytes, due to the anion coordinating effect of Lewis acidic compounds. In tribology, borate ester has also been suggested for effectively improving the friction-reducing and anti-wear properties of N-containing Lewis bases by the Lewis acid–base complex formation [20]. In this study, the Lewis acid (borate ester and boric acid) was introduced to enhance the structure strength and tribological performance of lithium grease under high temperature by the complex formation with Lewis base RCO_2^- of LHS [21]. Details about the Lewis acid–base complex were revealed by combination of TGA–DSC and FTIR measurements. Compared with the pure LHS, the complex displays better thermal stability. Furthermore, the Lewis acid center can serve as second-level linking point to enhance the strength of thickener fiber network and colloidal stability under high temperature, which was elucidated by means of rheological method.

Experimental section

Synthesis of lithium grease

The lithium grease was synthesized as detailed in our previous work [11]. The weight percentage of lithium soap was 11.5 wt%. Then, tributyl borate (TBB) was added into the base grease, mixed by mechanical stirring and ground five times on a triple-roller mill. The typical properties of synthesized grease with different TBB concentrations are reported in Table 1.

Characterization and property measurements

The tribological performance of the synthesized greases was evaluated via an Optimol-SRV IV oscillating friction and wear tester. The test was conducted in a conventional reciprocating “ball-on-block” mode with an oscillating upper ball (AISI E52100 steel, 10 mm in diameter, HV 710-730) and a fixed lower disk (AISI E52100, ø 24 mm × 7.9 mm, HV 710-730). MicroXAM 3D non-contact surface mapping profiler was employed to measure the wear volumes of the wear scars on the lower disks.

Rheological measurements were carried out on an Anton Paar MCR 302 rheometer (Austria) using plate to plate geometry (24.985 mm diameter and 1 mm gap). The amplitude sweep tests, at the temperature of 25 and 100 °C and the frequency of 1 Hz, were performed to characterize the strength of thickener fiber network. Shear experiments by varying the temperature from 25 to 100 °C and shear rate from 0.01 to 100 s^{-1} were carried out to reveal the evolution behavior of lubricating grease.

Fourier transform infrared spectroscopy (FTIR) measurements were performed to characterize the molecular structure of Lewis acid–base complex on an IFS 66v/S FT-IR spectrometer (Bruker, Germany) using the KBr disk method. The thermal stability of Lewis acid–base complex was evaluated by TGA–DSC (Netzsch, Germany).

Results and discussion

Tribological performance

In this paper, the influence of Lewis acid TBB on the high-temperature tribological performance of lithium grease is investigated. Fig. 1 shows friction coefficient curves of lithium grease with different TBB concentrations under different temperature, and the corresponding wear volumes of the lower disks were also measured to evaluate the anti-wear property via non-contact surface mapping profiler. Under room temperature, the short seizure of lithium grease is avoided when the TBB concentration is up to 1.5 wt% (Fig. 1a). Meanwhile, the wear volumes of the lower disks lubricated by additivated grease are reduced by 30%–50%, compared with that lubricated by base grease (Fig. 1c). Furthermore, the TBB displays greatly reinforcing effect on the tribological properties under high temperature. It can be observed that the lithium greases with the TBB concentration >1.5 wt% display excellent friction-reducing and anti-wear properties with 15% friction and 97% wear reductions, compared with that of base grease. The wear situations in the temperature ramp tests are further checked with optical microscope, as shown in Fig. 2. The wear surface of the disk lubricated by base grease shows considerably wider and deeper wear scar, indicating severe scuffing occurred. With increasing the TBB concentration, the wear situations are obviously improved. Wear scars lubricated by grease with TBB >3 wt% display very smooth trace and very little wear.

To further study the reinforcing effect of TBB on the high-temperature tribological performance, the load ramp tests, frequency ramp tests and fixed condition tests are conducted at 150 °C. Fig. 3a displays load ramp tests from 50 to 250 N for base grease and grease with 4.5 wt% TBB. The additivated grease exhibits similar load-carrying capacity with base grease. However, the friction-reducing property was obviously improved. During the frequency ramp tests (Fig. 3b), it shows similar tendency with the results in Fig. 3a and the additivated grease displays obviously lower friction coefficients for the entire test time. In addition, the long time friction tests at 150 °C are carried out to further evaluate anti-wear property as shown in Fig. 3c. We can see that additivated grease displays excellent friction-reducing and anti-wear properties with >40% friction and >95% wear reductions.

XPS analysis is used to verify the constituents of the tribofilm on the worn surface for exploring the mechanism of reinforcing effect of TBB (Fig. 4). The binding energies of B1s (Fig. 4a) at 193.6 eV and 192 eV correspond to the boron of H_3BO_3 and B_2O_3 [22,23]. Meanwhile, the main peaks of O1s appearing at 533.4 eV, 532.6 eV, 531.8 eV, 531.7 eV, and 530.1 eV can be attributed to the oxygen of H_3BO_3, B_2O_3 Fe(OH)O, FeOOH, and Fe_3O_4 [22–25]. Based on the XPS spectra of B1s and O1s, two boron compounds can be observed and the content of boric acid is higher. Moreover, the Fe2p peaks, appearing at 724.3 eV, 711.5 eV, 711.4 eV, 710.8 eV, and 724 eV, are

Table 1
Typical properties of synthesized grease with different concentrations of TBB.

Properties L/T mole ratio	0 wt%	1.5 wt% ≈6	3 wt% ≈3	4.5 wt% ≈2	6 wt% ≈1.5	Test method
Cone penetration (0.1 mm)	211	216	213	216	215	ASTM D217
Roll stability	+24	+20	+22	+26	+25	ASTM D1831
Dropping point (°C)	215	252	277	291	262	ASTM D556
Oil separation (%)	2.3	1.5	2.1	3.5	5.1	ASTM D6184

L/T mole ratio, the mole ratio between LHS and TBB.