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Tribological characteristics of monodispersed cerium borate nanospheres in biodegradable rapeseed oil lubricant

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ABSTRACT

Stearic acid-capped cerium borate composite nanoparticles, abbreviated as SA/$CeBO_3$, were prepared by hydrothermal method. The morphologies, element compositions, size distributions, crystal and chemical structures, hydrophobic characteristics, of SA/$CeBO_3$ were characterized by scanning electron microscope, energy dispersive X-ray spectrometer, dynamic laser particle size analyzer, X-ray diffraction, and Fourier transform infrared spectrometer, respectively. The friction and wear performances of SA/$CeBO_3$ as a lubricating additive in a rapeseed oil were evaluated on a four-ball tribo-tester. The tribochemical characteristics of the worn surfaces were investigated by X-ray photoelectron spectroscopy. The results showed that the hydrophobic SA/$CeBO_3$ were monodispersed nanospheres with an average diameter of 8 nm, and exhibited excellent dispersing stability in rapeseed oil. Meanwhile, SA/$CeBO_3$ nanospheres were outstanding in enhancing friction-reducing and anti-wear capacities of rapeseed oil. The prominent tribological performances of SA/$CeBO_3$ in rapeseed oil were attributed to the formation of a composite boundary lubrication film mainly composed of lubricous tribochemical species of B_2O_3, CeO_2 and Fe_2O_3, and the adsorbates of SA/$CeBO_3$ and rapeseed oil, on the tribo-surfaces.

1. Introduction

Over the past decades, nanoscale materials have been extensively investigated and widely employed in many scientific and technological fields due to their fascinating physical and chemical nature.[1–5] In tribological applications, much effort has also been made in developing efficient nanometric lubricant additives, in which inorganic nanospecies, such as metal sulphide [6,7], oxide [8–10], fluoride [11–13] and metal powders [14,15] have been of special interest. Indeed, many inorganic nano-particles have been proven to be promising as lubricant additives since they provided outstanding ability in reducing friction and wear when formulated into lubricants, although in practice, poor dispersancy of inorganic nanomaterials in lubricants is usually the main obstacle to restrict their satisfactory applications, and surface modification has to be done to overcome this weakness [16,17]. Unfortunately, among various nanometric inorganic lubricant additives, only a few reports are currently available about the friction and wear performances of rare earth compounds, which have been reported to provide excellent anti-wear and friction-reducing capacities because of their special physio-chemical properties [18–20]. It is thus of important tribological significance to further investigate the friction and wear behaviors of nanoscale rare earth compounds in lubricants.

Also in the past decades, environmentally friendly lubricants have spurred since contamination of eco-systems caused by conventional petroleum-based lubricants has posed great environmental problems mainly due to their unreadily biodegradable nature. Since the middle of the 1970s, focus on health, safety and the preservation of the environment has turned the searchlight to the effects of mineral lubricants on the environment and has stimulated the development of lubricants that show more or less compatibility with the environment [21–24]. The key issue in formulating environmentally friendly lubricant oils is the choice of reliable base oils and suitable performance additives. Nowadays, many base oils such as vegetable oils and synthetic esters have found practical applications in the formulation of biodegradable lubricants thanks to their excellent biodegradability and non-toxicity [25,26]. On the other hand, the development of alternatives to conventional lubricant additives such as zinc dialkyldithiophosphate (ZDDP) has also been a subject of significant interest, mainly due to environmental concerns arising from S and P elements in the additives. In recent years, special interests in nanoparticles as biodegradable lubricant additives have also been taken [19,27–30]. The present paper aims at exploring the possibility of nanoscale cerium borate as a lubricant additive and understanding its friction and wear behaviors in

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biodegradable rapeseed oil. Cerium borate nanospheres were prepared and their surfaces chemically modified with stearic acid to improve their dispersing ability in rapeseed oil. The tribological performances and mechanisms of cerium borate nanospheres in rapeseed oil were investigated.

2. Experimental

2.1. Preparation of stearic acid-capped cerium borate nanoparticles

3.4 g $Na_2B_4O_7 \cdot 10H_2O$ and 2.0 wt% of stearic acid were well dissolved into 60 mL distilled water under vigorous stirring. The resultant solution was marked as A. In addition, 2.6 g $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved into 60 mL anhydrous ethanol, and the resultant solution was marked as B. Then the solution B was added dropwise into solution A under agitation at the ambient temperatures. The pH values of the mixture were carefully adjusted to about 13 with diluted sodium hydroxide solution. After addition of solution B, the resultant mixture was kept on stirring for 1 h and then transferred into a 200 mL Teflon-lined stainless-steel autoclave filled with anhydrous ethanol up to 80% of the total volume, sealed and treated hydrothermally at 180 °C for 4 h. Thereafter, the treated mixture was cooled to room temperatures and centrifuged to obtain the precipitates, which were then washed repeatedly with distilled water and anhydrous ethanol, followed by drying at 80 °C for 4 h in air to obtain the white, stearic acid-capped cerium borate nanopowders (abbreviated as SA/$CeBO_3$). For comparison purposes, un-capped cerium borate ($CeBO_3$) nanoparticles were also prepared in the same procedures without addition of stearic acid in solution A.

2.2. Friction and wear tests

Different mass percentages of SA/$CeBO_3$ and $CeBO_3$ nanoparticles, as well as stearic acid, were separately dispersed ultrasonically into rapeseed oil (RP), and the friction and wear performances of the formulated oils and neat rapeseed oil were evaluated on a four-ball tribo-tester. The tribo-tester consists of a loaded rotating ball that glides on three fixed balls. For each test run, friction coefficients and wear scar diameters (WSD), which well characterize the friction and wear behaviors of a lubricant in the four-ball testing, were determined under the rotary speed of 1500 r/min and loads of 392 N for 30 min at room temperatures. The lower the friction coefficients and WSD, the better the lubricating properties of a lubricant are. The balls used in the present tests are GCr15 bearing steel balls 12.7 mm in diameter, 59–61 HRC in hardness and R_a 0.040 μm in surface roughness. Each run was repeated twice and the average was reported. Prior to the tests, the balls were cleaned in an ultrasonic bath with petroleum ether for 10 min and then dried with a hair dryer. After the tests, the tested balls were again ultrasonically rinsed in petroleum ether for 10 min for surface analysis purpose.

2.3. Characterization of nanoparticles and analysis of worn surfaces

The morphologies and the sizes of SA/$CeBO_3$ and $CeBO_3$ nanoparticles were characterized by an JEOL S-4800 field emission scanning electron microscope (SEM), and the element compositions of SA/$CeBO_3$ and $CeBO_3$ were determined by an energy dispersive X-ray spectrometer (EDS) attached to the SEM, while the particle size distributions were detected on a Nano ZS90 dynamic laser particle size analyzer by dispersing SA/$CeBO_3$ in anhydrous ethanol. Furthermore, the crystal and chemical structures of SA/$CeBO_3$ and $CeBO_3$ nanoparticles were characterized by a Rigaku Dmax-2500 X-ray diffraction (XRD; Cu Kα irradiation) and a Perkin-Elmer 400 Fourier transform infrared spectroscopy (FTIR), respectively. Moreover, the hydrophobic characteristics of SA/$CeBO_3$ and $CeBO_3$ were detected by measuring water contact angles on a Easydrop DSA14 contact angle goniometer, by pressing the samples into a wafer with an IR powder-pressing machine under 15 MPa for 2 min. Finally, the tribochemical species on the worn steel surfaces were analyzed by a Thermo ESCALab-250 X-ray photoelectron spectroscope (XPS), where the binding energy of the tested elements was measured at a pass energy of 29.4 eV and a resolution of ±0.3 eV, with the Al Kα radiation as the excitation source and the binding energy of contaminated carbon (C1s: 284.80 eV) as the reference.

3. Results and discussion

3.1. Characterization of nanoparticles

SEM images of $CeBO_3$ and SA/$CeBO_3$ nanoparticles are shown in Fig. 1. In Fig. 1(a), the $CeBO_3$ is sphere-like irregular with diameters in the range of 5−30 nm; while in Fig. 1(b), the SA/$CeBO_3$ displays a monodispersed spherical topography with an average diameter of about 10 nm. This indicated that stearic acid was responsible for the modification of cerium borate nanospheres and obviously reduced the agglomeration of cerium borate nanospheres.

EDS spectrum of the SA/$CeBO_3$ nanospheres is shown in Fig. 2. It can be observed from Fig. 2 that the peaks of elements Ce, B, O and C are obvious. Quantitative calculation indicated that the atomic ratio of Ce, B and O was 1:1.08:3.12, which was very close to the

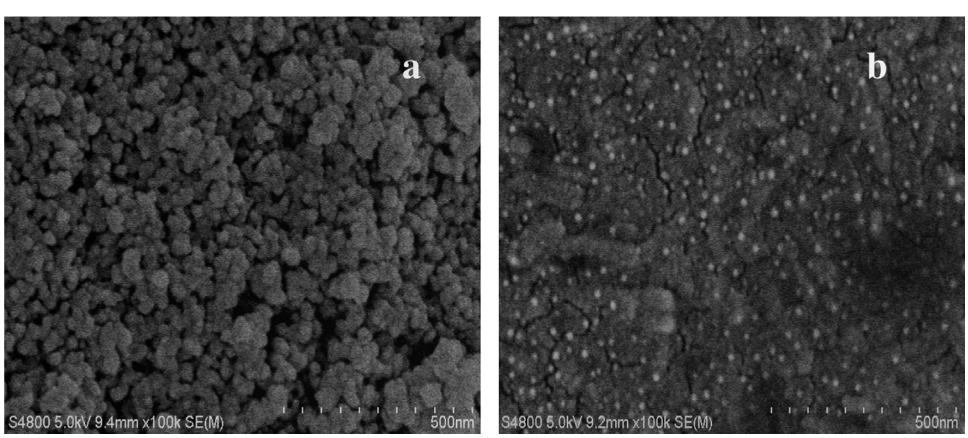

Fig. 1. SEM images of (a) $CeBO_3$ and (b) SA/$CeBO_3$.