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Tribological performance of Mg/Al/Ce layered double hydroxides nanoparticles and intercalated products as lubricant additives

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ABSTRACT

Mg/Al/Ce ternary layered double hydroxides (LDHs) were synthesized via coprecipitation and intercalated by succinic acid and lauric acid through ion exchange method respectively. The LDHs products were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and Fourier transform infrared (FT-IR). Tribological properties of LDHs as lubricant additives were evaluated by four-ball friction and air compressor test. The results indicated that Mg/Al/Ce LDHs were prepared successfully with Ce/Al molar ratio of 0.05 and crystallization temperature of 140 °C. The interlayer spacing of LDHs precursor was expanded by succinic acid and lauric acid to 8.838 and 17.519 Å respectively. All the three LDHs products can reduce friction and wear of engine lubricating oil in the tests. LDHs intercalated with lauric acid showed best tribological performance among them which was attributed to sliding each other between laminates, good dispersibility in oil medium and a protective tribofilm formed on the worn surface.

1. Introduction

In tribology field, nanoparticles as lubricant solid additives have been paid much attention in the past decades [1], like metals [2], graphite [3,4], metal sulfides [5–8], oxides [9], borates [10] and mineral powders [11,12]. Due to the nanoscale, ultrahigh specific surface area and chemical activity, nanoparticles exhibited excellent friction-reducing, anti-wear, extreme pressure and self-repairing properties under boundary lubrication condition compared with other additives.

It was investigated that rare earth compounds could also improved the tribological properties of lubricating oil as additives [13–16]. Zhou et al. [13] studied that LaF_3 nanoparticles improved load-carrying and anti-wear capacity of liquid paraffin. It was attributed to the boundary film formed on the worn surface which consisted of LaF_3 nanoparticles depositing film and tribochemical reaction film with the elements of S and P. Liu et al. [16] found that mixed rare earth nanoparticles formed a protective film which was composed with ferrous oxides, rare earth oxides and complex of rare earth metals on the friction surface. Oxidation catalysis of rare earth led to high concentration of ferrous oxides on the surface which contributed to the excellent friction-reducing properties.

Layered double hydroxides (LDHs) nanoparticles have been proved to possess excellent tribological performance as lubricant additives which they can reduce friction coefficient and size of wear scars to protect the rubbed surface effectively [17–20]. In this work, Mg/Al/Ce ternary layered double hydroxides (MAC-LDHs) nanoparticles were synthesized with discussing the effect of Ce^{3+}/Al^{3+} molar ratio. LDHs were intercalated with succinic acid (SA) and lauric acid (LA) respectively. The tribological properties of LDHs precursor and intercalated products as lubricant additives were investigated and results showed that all the three LDHs products could reduce friction coefficient, wear scar diameter of engine lubricating oil and consumption of motor at different levels. Especially the LDHs intercalated with long-chain agent (lauric acid) exhibited best friction-reducing performance.

2. Experiment

2.1. Synthesis of LDHs nanoparticles

$Mg(NO_3)_2·6H_2O$, $Al(NO_3)_3·9H_2O$, $Ce(NO_3)_3·6H_2O$, NaOH and Na_2CO_3 were analytical grade without further purification and commercially available. Deionized water was prepared in the laboratory. LDHs were prepared by coprecipitation method [21,22]. The three nitrates were mixed and dissolved in deionized water with total metal cation molar concentration 2 mol L^{-1}. Four solutions were designed with different Ce^{3+}/Al^{3+} molar ratio ranging

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Table 1
Typical properties of engine lubricating oil.

Engine lubricating oil	Kinematic viscosity (mm^2/s)		Viscosity index	Open flash-point (°C)	Boiling point (°C)
	40 °C	100 °C			
Diesel engine oil (CD 15W-40)	110.60	15.02	141	228	300

from 0.00, 0.05, 0.15 to 0.25 respectively which had consistent $Mg^{2+}/(Al^{3+} + Ce^{3+})$ molar ratio of 2:1. A mixed alkaline solution of NaOH and Na_2CO_3 with OH^- molar concentration 4 mol L^{-1} was added dropwise at 5 ml min^{-1} to stirred salt solution till the final pH value reached 11 at room temperature and then stirring for 60 min. The slurry was aged at 140 °C for 15 h in an autoclave. Finally the precipitate was filtered and washed with deionized water and ethyl alcohol until pH reached 7 and dried at 80 °C for 12 h. The four samples with Ce^{3+}/Al^{3+} molar ratio of 0.00, 0.05, 0.15 and 0.25 were signed as M_2A-LDHs, $M_{2.1}(AC_{0.05})$-LDHs, $M_{2.3}(AC_{0.15})$-LDHs and $M_{2.5}(AC_{0.25})$-LDHs respectively.

2.2. Intercalation of MAC-LDHs

Two intercalating agents, succinic acid ($HOOCCH_2CH_2COOH$) and lauric acid [$CH_3(CH_2)_{10}COOH$] were analytical grade without further purification. The agents were intercalated to MAC-LDHs by ion exchange method respectively. The mixed powders with agent/LDHs molar ratio of 2:1 were added to 500 ml deionized water and stirred till turned to be homogeneous and then the slurry was adjusted and maintained pH value 5 with hydrochloric acid for 3 h at 80 °C. Eventually the precipitate was filtered and washed with hot deionized water and ethyl alcohol till pH reached 7 to remove the remaining agents totally and dried at 80 °C for 12 h. The products intercalated by succinic acid and lauric acid were signed as MAC-SA-LDHs and MAC-LA-LDHs respectively.

2.3. Characterization of LDHs nanoparticles

All the LDHs were analyzed by X-ray diffraction (XRD) with Rigaku diffractometer (CuKα source, λ = 0.15406 nm, operated at 40 kV and 100 mA, scanning rate 8° min^{-1} from 3° to 70° (2θ)). The Fourier transform infrared (FT-IR) spectroscopy was recorded on a NICOLET750 FT-IR spectrometer (4000–450 cm^{-1}, KBr sheet). The morphology of LDHs were observed on a scanning electron microscope (SEM; JSM-6460LV, JEOL, Tokyo, Japan) connected with energy disperse spectroscopy (EDS) at an acceleration voltage of 20.0 kV. The particle size distribution of MAC-LDHs was measured by Zetasizer (Nano ZS90, Malvern).

2.4. Tribological properties of LDHs nanoparticles as lubricant additives

The friction property test was conducted on a MS-10JR four-ball friction tester and the balls with diameter of 12.70 mm and hardness of 64–66 HRC were made of GCr15 steel (AISI 52100 steel, 0.95–1.05% C, 1.30–1.65% Cr, 0.15–0.35% Si, 0.25–0.45% Mn, ≤0.027% P, ≤0.02% S, ≤0.23% Ni, ≤0.25% Cu) and cleaned by petroleum ether and ethyl alcohol for 10 min in an ultrasonic cleaner before the test. Three kinds of LDHs products (MAC-LDHs, MAC-SA-LDHs and MAC-LA-LDHs) were ground with Span 60 powders (mass ratio of 1:1) for 30 min respectively [11] before added to engine lubricating oil (Table 1) with the consistent amount of 0.5 g LDHs per 100 ml oil [19]. Then three oil samples were stirred under high speed agitator (10,000 rpm) and ultrasound at 80 °C for good dispersibility respectively. The test was conducted under the rotating speed of 1200 rpm and load of 392 N for 60 min at room temperature [17,19]. For reliability of results, the friction test was repeated for three times at total same conditions. The coefficient of friction was recorded in a computer by the sensor connecting with tester. The average coefficient was calculated with the data after 15 min and average wear scar diameter of 3 lower balls was determined by an optical microscopy.

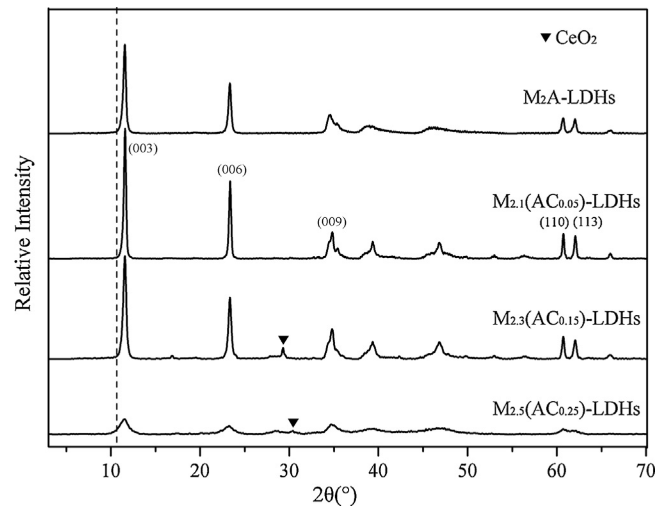

Fig. 1. XRD patterns of four LDHs samples with different Ce/Al molar ratio, M_2A-LDHs, $M_{2.1}(AC_{0.05})$-LDHs, $M_{2.3}(AC_{0.15})$-LDHs and $M_{2.5}(AC_{0.25})$-LDHs.

The air compressor (Model Dingwei ZB-0.11/7) is used to output pneumatic power through transforming mechanical energy of piston motion to energy of gas pressure. Lubricating oil could reduce friction between piston and cylinder wall contributing to the decrease of power consumption of driving motor and oil temperature which were measured by Model 8705B power meter and JM222 thermometer respectively. Therefore, the test can demonstrate the tribological properties of LDHs indirectly. The rotating speed of motor was 2850 rpm with test duration of 20 min and all the three kinds of LDHs products were added to engine lubricating oil with the same content and treatment method as four-ball friction test respectively.

3. Results and discussion

3.1. X-ray diffraction and morphology of LDHs

The XRD patterns of synthetic LDHs with different Ce/Al molar ratio were shown in Fig. 1. From the XRD patterns, all the four LDHs samples showed typical layered structure diffraction peaks (0 0 3) and (0 0 6) of hexagonal symmetry phase. The narrow and sharp peaks of M_2A-LDHs and ternary $Mg_{2.1}(AlCe_{0.05})$-LDHs showed high crystallinity and peak (1 1 0) represented the perfect internal structure of brucite-like layers [23]. As the Ce/Al ratio equaled to 0.15, the peak of impurity which could be distinguished as CeO_2 appeared at 2θ = 29.28° in spite of the high degree of crystallization [24,25]. However, as the Ce/Al molar ratio rose further, the diffraction intensity of $M_{2.5}(AC_{0.25})$-LDHs weakened dramatically and peaks shape turned to be very low and wide due to the distortions of octahedrons in the laminates after substitution of more Al^{3+} (ionic radius = 0.53 Å) by larger Ce^{3+} (ionic radius = 1.02 Å) [21,22,26].