Friction behavior of Mg–Al–CO$_3$ layered double hydroxide prepared by magnesite

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A B S T R A C T

In this paper, Mg–Al–CO$_3$ LDH was prepared by magnesite under chemical precipitation and hydrothermal methods. In order to improve the dispersion of LDH in base oil, the as-prepared sample was modified with sodium laurate. The obtained material (GMAC-LDH) was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry and thermo gravimetric analyzer (DSC–TGA) and scanning electron microscope (SEM). The results show that the modified LDH has platelet morphology with a near hexagon shape. In addition, the tribological properties of GMAC-LDH were evaluated by four-ball friction tester and gear tester. As a lubricant, GMAC-LDH possesses an excellent property on reducing friction and wear of friction pair. The results of friction tests indicated that the friction coefficient, diameter of wear scar and power consumption of the oil with GMAC-LDH was reduced by 11.0%, 8.5% and 2.1% as compared with that of base oil.

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1. Introduction

In recent years, the exploration of nanoparticles used as lubricant materials has received considerable attention owing to their unique properties in anti-wear, reducing friction, and the endurance under extreme pressure [1–3]. Many studies on solid particles, such as elementary substance [4,5], oxides [6,7], borate [8] and layered silicate minerals used as lubricant additives have been reported. In some papers, serpentine was served as anti-frictional and self-repairing materials. According to the experimental results, serpentine could significantly reduce friction coefficient and wear of friction pairs. Yu [9] found that the addition of 1.5 wt% serpentine (layered silicate mineral) to oil with the load at 100 N could decrease the friction coefficient by 50.6% and the wear rate of disk specimen by 82.3% as compared to pure oil. On the basis of Zhao [10], the friction coefficient of base oil with 0.5 wt% serpentine could be reduced by 21.83% compared with the base oil. Although the serpentine has superior performance in reducing friction coefficient and anti-wear, the processes, such as ultrafine powders, surface modification and activating treatment, may be complex before natural minerals are used as anti-frictional and self-repairing materials. In addition, the particle size of serpentine is difficult to control [11]. The materials with simple synthesis process and controlling granulation are needed to be utilized as lubricant material.

Layered double hydroxides (LDHs), also known as anionic or hydrotalcite-like clays, are a class of layered compounds that consist of positively charged brucite-like host layers and hydrated exchangeable anions located in the interlayer gallery for charge balance. The charge of the brucite-like layers was due to the iso-morphous substitution of a part of the divalent metal ions by trivalent ones [12]. The general chemical composition of LDH is [M$^{2+}_{2x-1}$,M$^{3+}_x$(OH)$_2$]$^{2x+}$(A$^{-n}$)$_n$mH$_2$O, where M$^{2+}$ and M$^{3+}$ are divalent and typically trivalent metal cations respectively on the layer; x is the molar ratio of the trivalent cation [M$^{3+}$/2(M$^{2+}$+M$^{3+}$)]; A$^{-n}$ is the interlayer anions with the charge n and m is the amount of H$_2$O interlayer. LDHs have been found in a wide variety of uses, such as adsorbents, catalysts, catalyst supports, biosensors and magnetic materials [13–15]. Recently, the LDH used as lubricant additive was reported. Fu [16] reported that the friction coefficient of oil with Cu–Mg–Al–CO$_3$ LDHs could be reduced 32% in comparison with base oil. Bai [11] delivered a paper about the frictional performances of Co–Al–CO$_3$ layered double-metal hydroxides. The result indicated that Co–Al-LDHs could significantly reduce friction coefficient and energy consumption of driving motor by 49.1% and 7.0% respectively. The experimental result of Zhao [17] shown that the Mg–Al–CO$_3$ LDH prepared by chemical reagents has excellent property in friction-reduce, with the friction coefficient decreased by 23.8% comparing with base oil. In addition, LDHs were easy obtained by many ways [18–21], the granularity of which could be also controlled through synthetic conditions. Because of these advantages, LDHs may be widely used as lubricant material.

In this paper, Mg–Al–CO$_3$ layered double hydroxide prepared with magnesite was modified by sodium laurate solution to
improve the dispersion in base oil. The modified sample was used as lubricant material.

2. Experimental and characterization methods

2.1. Materials

Magnesite was obtained from Haicheng of Liaoning province. All chemical reagents, including aluminum nitrate hydrate (Al(NO3)3·9H2O), sodium hydroxide (NaOH), nitric acid (HNO3) and sodium laurate (C12H23O2Na), used in the experiment were analytical grade and without further purification. Deionized water (18 MΩ/cm) was employed throughout this work.

2.2. Synthesis of Mg–Al–CO3 LDH and surface modification

The chemical precipitation and hydrothermal methods [22], as Fig. 1 showed, was utilized to synthesize Mg–Al–CO3 LDH with the molar ratio of magnesite and Al(NO3)3·9H2O at 2.5:1, the aging time of 16 h and crystallization temperature of 100 °C. The prepared sample was modified by sodium laurate solution at the temperature of 60 °C, the pH around 7.0 under stirring for 2 h to obtain GMAC-LDH.

2.3. Characterization of LDHs

X-ray diffraction (XRD) patterns of all samples were collected on a Rigaku D/max-RA powder X-ray diffractometer with Cu Kα radiation (λ = 0.154056 nm) at a scanning rate of 8°/min from 3° to 70°. Infrared spectra are recorded by KBr disks using a NICOLET750 FTIR instrument. The electron microscopic images were obtained on a BACPCS–4800 field emission scanning electron microscope at an acceleration voltage of 15 kV. Thermal analyses were performed with a DSC–TGA thermal analyzer (DuPont 1090B) at a typical rate of 10 °C/min.

2.4. Measurement of tribological properties

The lubricating oil (CD15W-40) with boiling point of 300 °C, viscosity 110.6 mm²/s at 40 °C, viscosity 15.2 mm²/s at 100 °C and viscosity index of 228, was used as base oil. The friction and wear tests were carried out on a four-ball tester (MR5-10A). The ball with a diameter of 12.7 mm and hardness of 59–61 HRC, is made of GCr15 steel. The parameters of four-ball tester were set as the speed of 1200 rpm/min with the loading of 392 N under room temperature for 1 h. 200 ml base oil with prepared GMAC-LDH concentration of 1 g/100 ml were added the tester. The wear mark diameter was determined by an optical microscopy.

![Fig. 1. The preparation process of Mg–Al–CO3 LDH with magnesite.](image)

There is an ND71e capacitor operation motor in the gear testing machine. The test is conducted at a speed of 2800 rpm/min loading at 45 N for 10 h. The concentration of LDHs was 1 g/100 ml base oil.

3. Results and discussion

3.1. X-ray diffraction of LDHs

As showed in Fig. 2, the GMAC-LDH was composed of Mg–Al–CO3 LDH and Mg–Al–C12H23O2 LDH [17]. The interaction between layer and interlayer anion was electrostatic attraction. When Mg–Al–CO3 LDH was modified by C12H23O2Na, C12H23O2− could replace some CO32− and enter the interlayer of LDH forming Mg–Al–C12H23O2 LDH.

![Fig. 2. The XRD patterns of LDHs. (A) Mg–Al–CO3 LDH; (B) GMAC-LDH.](image)

3.2. FT-IR spectroscopy of GMAC-LDH

In order to analyze the formation of GMAC-LDH, the infrared spectrum was recorded as Fig. 3 shown. A intense peak at 3486 cm⁻¹ was observed, attributing to the hydroxyl groups stretching mode from laminate and the interlayer water molecules

![Fig. 3. FT-IR spectroscopy of GMAC-LDH.](image)
[23]. The peaks located at 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\) were caused by symmetric stretching vibration of C–H [6]. To the contrary, the band at 1462 cm\(^{-1}\) was due to the anti-symmetric stretching vibration of C–H. A stretching vibration of C=O was recorded at 1750 cm\(^{-1}\). The sharp band observed around 1367 cm\(^{-1}\) was attributed to the \(\nu_3\) vibration of the CO\(_3^{2-}\) [24]. In addition, the \(\nu_4\) vibration of CO\(_3^{2-}\) was signed at 673 cm\(^{-1}\).

Through the above analysis, the anion in the interlayer of GMAC-LDH was C\(_{12}H_{23}O_2^-\) and CO\(_3^{2-}\). That was consistent with the XRD result.

3.3. Scanning electron microscopy of GMAC-LDH

Morphological information characterized by scanning electron microscopy (SEM) is shown in Fig. 4. The crystal morphology of modified LDH displays platelet-like structure with a hexagonal shape. Fig. 4(B) shows that the obtained product has a narrow distribution and the disk diameter of GMAC-LDH is mostly around 150 nm.

3.4. The thermal analysis of GMAC-LDH

The TGA and DSC curves of GMAC-LDH (a) and Mg–Al–CO\(_3\) LDH (b) were displayed in Fig. 5. Obviously, the TGA curve of GMAC-LDH could be divided into three parts for 35–200 °C, 200–500 °C and 500–800 °C. In the first stage, there was an endothermic peak at 200 °C (the corresponding peak in Fig. 5(b) was at 221 °C) that was due to the loss of interlayer water. The weight loss was 10.6% in this stage, that mainly owing to lose the absorbed and interlayer water. In the second stage, the oxidation of sodium laurate absorbed on the surface of LDH, decomposition of hydroxyl in the laminate and the removal of C\(_{12}H_{23}O_2^-\) and CO\(_3^{2-}\) interlayer lead to the weight loss which was reduced severely by 54.8%. The exothermic peak at 250 °C was ascribed to the oxidation of sodium laurate absorbed on the surface of LDH. Comparing with Fig. 5(b), there was an endothermic peak at 485 °C in Fig. 5(a), which may be attributed to the removal of C\(_{12}H_{23}O_2^-\) interlayer. In Fig. 5(a), an endothermic peak at 314 °C was attribute to the decomposition of hydroxyl in the laminate of Mg–Al–CO\(_3\) LDH [17]. Similarly, the peak at 367 °C may be due to the decomposition of hydroxyl in the laminate of Mg–Al–C\(_{12}H_{23}O_2\) LDH. The weight loss was 3.5% in the last section. That was due to the removal of surplus CO\(_3^{2-}\) interlayer [22]. In the process of thermal decomposition, the total weight loss was 68.9%.

3.5. Friction performances of GMAC-LDH

3.5.1. Four-ball friction tests

Fig. 6 illustrates the friction coefficient curves of lubricating oil with and without LDHs. At the beginning, there was a little difference between base oil (MY) and base oil containing GMAC-LDH (GMAC). After running 20 min, the distance of two curves started increasing. The average friction coefficient of MY is 0.109 within 60 min. In the same conditions, the average friction coefficient of GMAC (0.097) reduced by 11.0% compared with MY. In addition, as Table 1 shows that the average diameter of steel balls

![Fig. 4. The SEM imagines of GMAC-LDH. (A) High magnification; (B) low magnification.](image)

![Fig. 5. The DSC–TGA curves of samples. (a) GMAC-LDH; (b) Mg–Al–CO\(_3\) LDH.](image)

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wear scar diameter (mm)</th>
<th>Average</th>
<th>Reduction compared with base oil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil</td>
<td>0.49 0.52 0.54</td>
<td>0.517</td>
<td>-</td>
</tr>
<tr>
<td>GMAC-LDH</td>
<td>0.45 0.46 0.51</td>
<td>0.473</td>
<td>8.5%</td>
</tr>
</tbody>
</table>
in the system with GMAC-LDH (0.473 mm) decreased by 8.5% as compared with base oil (0.517 mm). The results indicated the wear resistance of oil with GMAC-LDH powder is better than that of the base oil [25].

3.5.2. Gear test

Fig. 7 shows the correlation between power consumption and the testing time during the gear test. The curve of GMAC increased at the beginning and then decreased as the extension of running time. After running 420 min, the values between two curves were going to be different. The average power consumption of driving motor reduced by 2.1% with the GMAC-LDH added in the base oil within total 600 min.

The tribological mechanism of LDHs was similar to the serpentine [11]. The surface of LDHs with metal cation can be easily absorbed on the friction pair. At the beginning of friction test, the particle of LDHs may increase friction due to the shearing effect between layers. After the smooth film of LDHs formed on the rubbing surface, the friction would start being reduced. The trend of the GMAC curve in Figs. 6 and 7 was the evidence of what had been discussed above.

4. Conclusion

In this paper, Mg–Al–CO$_3$ LDH was prepared with magnesite under chemical precipitation and hydrothermal methods. In order to improve the dispersion of LDH in base oil, the prepared sample was modified by sodium laurete. The test results show that the crystal morphology of modified LDH displays a platelet-like structure with a hexagonal shape and the diameter of particles is mostly around 150 nm. Thermal analysis indicated that the total weight loss was 68.9% in the range of 35–800°C.

GMAC-LDH possesses an excellent property of friction and wear reducing. As compared with base oil, the friction coefficient, diameter of wear scar and power consumption of the oil with GMAC-LDH was reduced by 11.0%, 8.5% and 2.1%. The excellent properties of LDHs make them become a potential lubrication and anti-frictional materials.

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References


