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Preparation and tribological properties of GO supported MoO_3 composite nanomaterials

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The MoO_3/GO composites were synthesized via a hydrothermal method. The performance of these composites as lubricating oil additives was investigated by a multifunctional friction testing machine. And the lubrication mechanism of MoO_3/GO in base oil was discussed based on SEM and EDS test data. The results demonstrate that MoO_3/GO composites as additives exhibit excellent anti-friction and anti-wear properties. This is mainly due to the synergistic effect between the lubricating film formed by the composite material on the wear surface and the self-healing ability of nano-MoO_3, which can effectively fill and repair wear scars while reducing friction and wear on the steel disc surface.

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1. Introduction

Many links in modern industrial production are affected by friction. It is estimated that approximately 20% of the world's total energy is wasted annually due to friction, while about 80% of mechanical part failures can be attributed to wear caused by friction. The detrimental impact of friction-induced wear on productivity in modern industry cannot be overlooked. In order to minimize the adverse effects of friction, the utilization of lubricants on mechanical sliding and rotating surfaces is a key measure to reduce wear[1-5]. In recent decades, numerous researchers have investigated the application of nanomaterials in lubricants to enhance their tribological properties. These nanomaterials include carbon-based materials, metal oxides, sulfides, nitrides, and pure metals. However, most existing studies mainly focus on the tribological properties of single nanomaterial additives. To meet practical engineering requirements, it is necessary to explore the synergistic effects of multiple nanomaterials in friction reduction and anti-wear. MoO_3 is considered a potential lubricant material due to its two-dimensional (2D) nature and extensive use in the field of friction [6-7]. Jian[8] found that using nano-MoO_3 as an additive can enhance the friction reduction and extreme pressure resistance properties of lubricating oil, which plays a key role in the lubricating film formed during the lubrication process. Wei[9] employed a multifunctional friction testing machine to investigate the tribological characteristics of layered

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MoO_3 as an additive. The findings indicate that optimal friction performance is achieved at a concentration of 0.1 wt%, which promotes synergistic effects between the physical film and friction film formed throughout the friction process.

Graphene's ultra-thin sheet structure, excellent mechanical properties and self-lubricating properties have attracted widespread attention in the field of friction[10-14]. It is currently used as a wear-resistant material, friction reducer and high-performance nano lubricant additive. Sudesh[15] studied the tribological properties of graphene oxide (GO) using a multifunctional friction machine in a reciprocating friction manner. The findings demonstrate that GO plays a key role in reducing friction and wear. Ruibin [16] synthesized novel graphene quantum dots (GQDs) via hydrothermal method and utilized them as additives, resulting in a significant decrease in both friction coefficient and wear rate within an optimal GQD concentration range. Due to their small size, uniform morphology, and abundant hydrophilic functional groups, GQDs act as water-soluble additives that can readily accumulate on the contact surface, forming an effective lubricant film and substantially enhancing the tribological performance of the lubricant. Hiroshi [17] employed the ball disc friction method to investigate the friction properties of graphene oxide (GO) and observed a significant enhancement in lubricating properties when GO was used as an additive. In summary, GO shows good potential as a lubricant additive in reducing friction and surface wear.

The use of MoO_3 and GO alone as additives showed good friction reducing properties. Previous research has shown that combining nanomaterials with graphene can not only enhance their inherent properties, but also stimulate new properties due to the synergistic effect between materials[18-19]. However, the application of GO and molybdenum trioxide composites in lubricants remains to be explored. In this paper, MoO_3/GO composite materials were synthesized by hydrothermal method, and their tribological properties were further studied through ball-disk friction experiments. In addition, the wear surface characteristics are analyzed and the lubrication mechanism is preliminary discussed.

2. Experimental

2.1. Material

Graphene oxide (GO) was purchased from Shenzhen Suiheng Technology Co., Ltd. Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$), sodium chloride (NaCl) and anhydrous ethanol (C_2H_5OH) were supported by Sinophosphate Chemical Reagent Co., Ltd. Chongqing Chuandong Chemical Co., Ltd. supports concentrated hydrochloric acid (36%-38%). The base oil (HW) is a 1:1 mixture of hydrogenated polydecene and distilled water.

2.2. Synthesis of MoO_3/GO nanocomposites

The MoO_3/GO nanocomposites are synthesized by a simple hydrothermal reaction. A typical process is to dilute concentrated hydrochloric acid with a mass fraction of 36%-38% at a volume ratio of 1:5 to a concentration of approximately 2mol/L. Disperse 0.24g sodium molybdate, 0.03g NaCl and 8ml dilute hydrochloric acid into 16ml deionized water (H_2O) using a magnetic stirrer. Then, 0.05 g of GO was added to the above solution and stirred vigorously for 60 minutes. Next, the stirred solution was transferred to a hydrothermal reactor with a volume of 50ml. After hydrothermal reaction at 190°C for 5h, the products were cooled to room temperature, centrifuged and washed three times with deionized water and anhydrous ethanol respectively. Finally, the centrifuged black samples were placed in a drying oven and kept at 80°C for 10h to obtain MoO_3/GO nanocomposites.

2.3. Preparation of lubricants

The preparation procedure of MoO_3/GO lubricating oil additive is shown in Fig.1. First, the MoO_3/GO nanomaterials were mechanically stirred into the HW liquid in a predetermined ratio. Then, Span*80 (S80) was added dropwise to the solution and stirred using a magnetic stirrer for 30 minutes to obtain a dispersed solution. Glycerol was then gradually added to increase the viscosity of the liquid. Finally, the mixed solution was dispersed ultrasonically for 30 minutes.

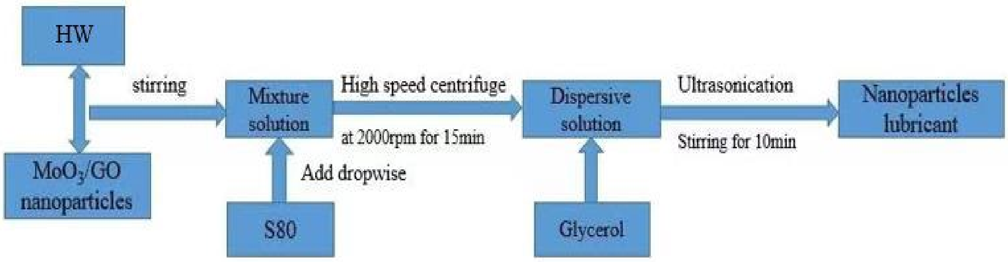

Fig. 1. Preparation flow chart of MoO_3/GO nano-additive lubricant.

2.4. Materials characterization

Powder X-ray diffraction (XRD) patterns were recorded by using a D8 advance (Bruker-AXS) diffractometer with Cu Ka radiation (λ=0.1546 nm). The 2θ range used in the measurement was from 10 to 80° with a velocity of 5° min^{-1}. The morphologies were investigated with a JEOL JSM-7001F field scanning electron microscope (FESEM) equipped with energy-dispersive spectrum (EDS) operated at an acceleration voltage of 20 kV.

2.5. Tribological properties measurement

The tribological properties of the oil containing MoO_3/GO composites were investigated via a MDW-02 reciprocating friction and wear testing machine. The schematic diagram of the testing principle of the ball-on-disk friction testing machine is shown in Fig. 2. The upper sample used in the experiment is a GCr15 steel ball with a diameter of 6mm and a hardness value of 770HV. And the counterpart is 45# steel disc of with size of Φ30 mm×5 mm in size. Clean the steel balls and discs with ethanol before testing. The experiments were performed at ambient temperature, and each experiment was repeated three times to obtain the average coefficient of friction (COF) value.

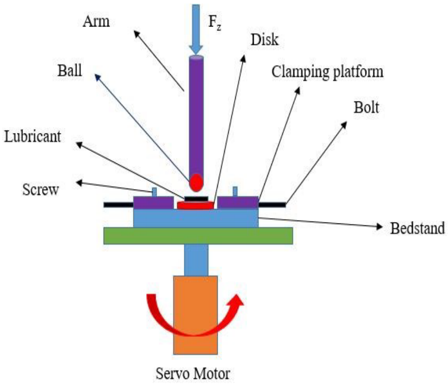

Fig. 2. Diagram of ball-disc friction.

3. Results and discussion

3.1 Structural and Morphological Characterization of MoO_3/GO

The XRD patterns of GO, MoO_3, and the MoO_3/GO composite nanomaterials are shown in Fig. 3. By comparing the XRD pattern of pure MoO_3 with the standard PDF card (JCPDS No. 35-0609), it can be observed that the diffraction peaks in the spectrum correspond to those of pure MoO_3, indicating good crystallinity of the prepared product. In addition, analysis of the XRD pattern for the composite reveals the diffraction peaks at 12.8°, 23.3°, 25.7°, 27.3°, 39.0°, 45.8°, and 58.8° which can be assigned to the (020), (110), (040), (021), (060), (200) and (081) lattice planes. Furthermore, compared with MO_3, the (020), (040), and (060) crystal planes of the composite material are significantly stronger. Therefore, the preferred growth directions for crystals in the composite are along the (020), (040) and (060) planes. The diffraction peak intensity belonging to GO (004) peak at 2θ=26.2° is sharp and distinct, but it weakens significantly in the composite due to graphene-molybdenum trioxide interaction that disrupts graphite's inherent properties. As a result, the characteristic peaks of graphene in the composite material become relatively weak.

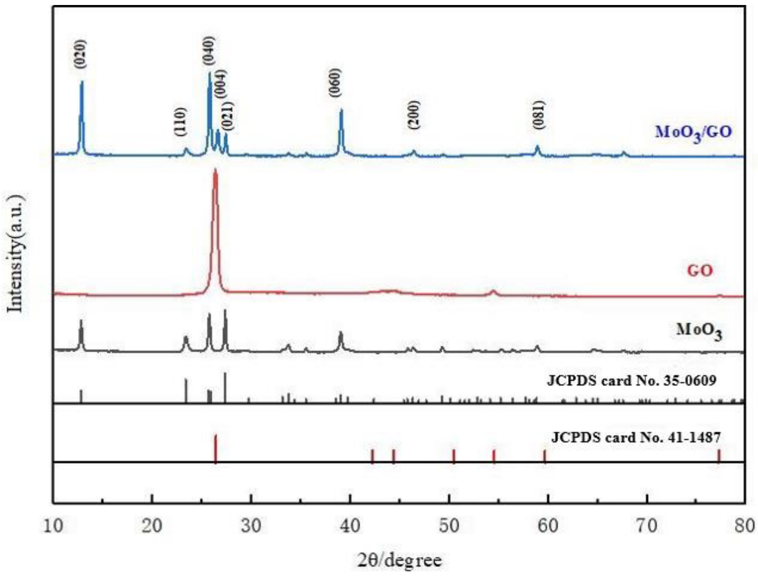

Fig. 3. XRD comparison pattern analysis of GO, MoO_3 and MoO_3/GO nanomaterials.

The SEM morphology images in Fig. 4a and b depict MoO_3 prepared by the hydrothermal method, exhibiting a larger number of nanoribbons with uniform thickness. The prepared nanoribbons are about 3um in length, uniform in size and densely distributed. Fig. 4c and d show SEM morphology images of GO at different magnifications, showing a uniform sheet-like structure with slight edge folding and an obvious gossamer-like texture in the center. The morphology of the MoO_3/GO composite material is shown in Fig. 4e and f. From the figures, it can be seen that a large amount of MoO_3 is tightly attached to the graphene surface. However, there still exists a significant gap between adjacent graphene sheets similar to that observed in pristine graphene material prior to recombination.

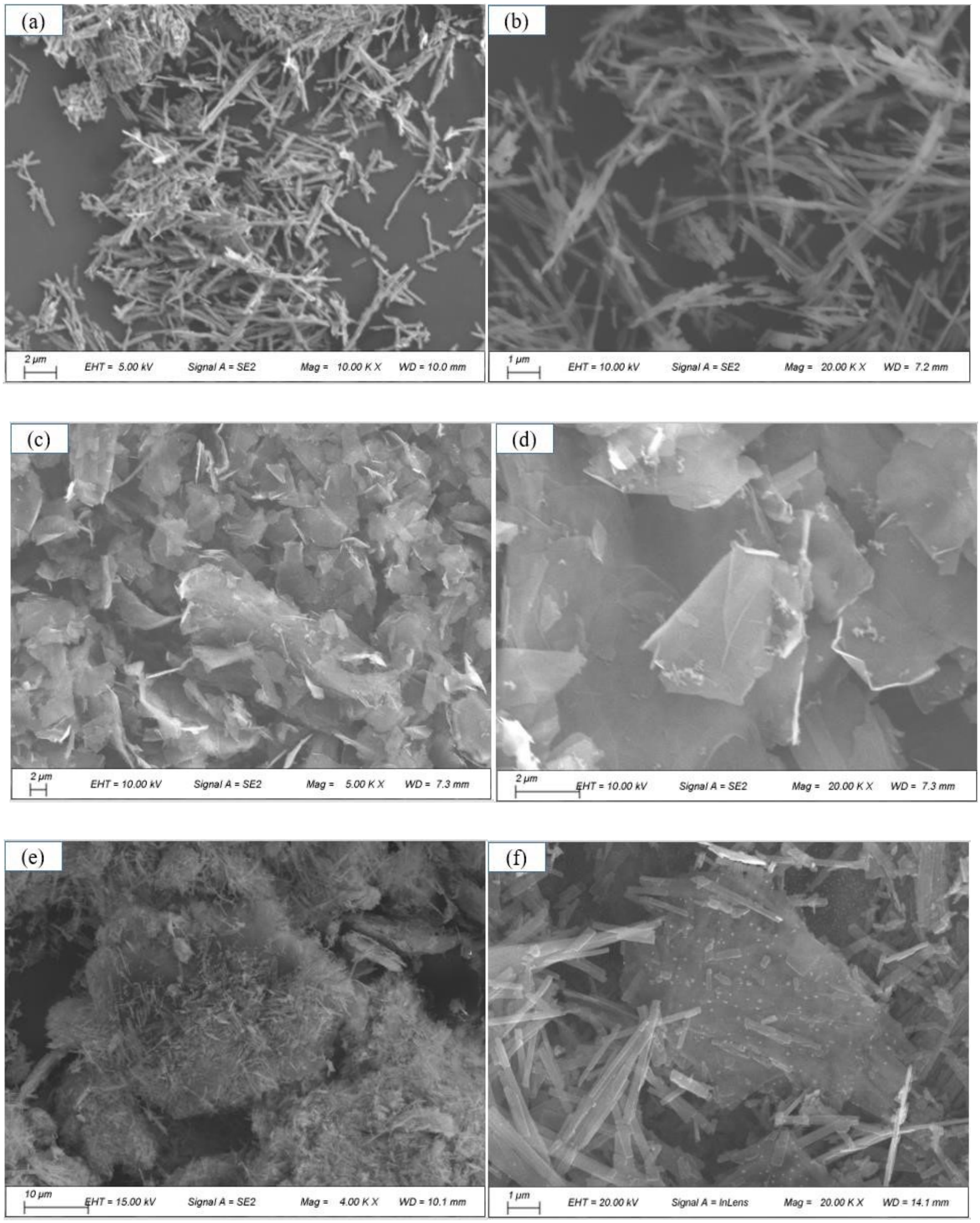

Fig. 4. SEM image of MoO_3 (a,b) , GO (c,d) and MoO_3/GO composites (e,f).

3.2. Tribological properties of MoO_3/GO

The MDW-02 reciprocating friction and wear testing machine was used to study the performance of lubricating oil containing MoO_3/GO nanomaterials with different mass fractions (0%, 0.5 wt %, 1.0 wt%, 1.5 wt%, 2 wt%) at room temperature, load 25N, speed 20mm/s and duration 600s. Fig. 5a shows the effect of the nanomaterial additive concentrations on the friction coefficient. It can be seen that the initial friction coefficient of the base oil is low in the early stage of the friction test, but as the working time increases, the friction coefficient gradually increases until it reaches a peak around 150 s, and then fluctuates within a certain range. Notably, the addition of MoO_3/GO nanoparticles significantly enhanced the friction reducing properties of the sliding interface compared with the results observed with the base oil. Among them, when the additive content is 0.5wt%, the friction coefficient decreases significantly, but the fluctuation is large. When the additive content reaches 1wt%, the friction coefficient also decreases significantly, and the friction coefficient tends to be stable after 100 s. Similarly, the change trend of friction coefficient when the additive concentration is 1.5 wt% is roughly consistent with that when the additive concentration is 0.5 wt%. However, when the additive content is 2.0wt%, the friction coefficient increases significantly. The main reason for the above phenomenon is that when the additive concentration is 0.5 wt%, the composite material insufficiently fills the surface wear of the friction pair, resulting in unstable friction coefficient and large fluctuations. When the additive content increases to 2wt%, the nanomaterials agglomerate, resulting in poor friction reduction effect.

The wear rate of the steel disc after the test is shown in the Fig. 5b. It can be seen from the figure that adding MoO_3/GO as an additive to lubricating oil can significantly reduce wear. It is worth noting that when the additive content reaches 1 wt%, the wear volume decreases to 10×10^{-5} cm^3. Compared with the base oil, the wear volume is significantly reduced by about 42%, thus proving the good anti-wear properties of the MoO_3/GO composite.

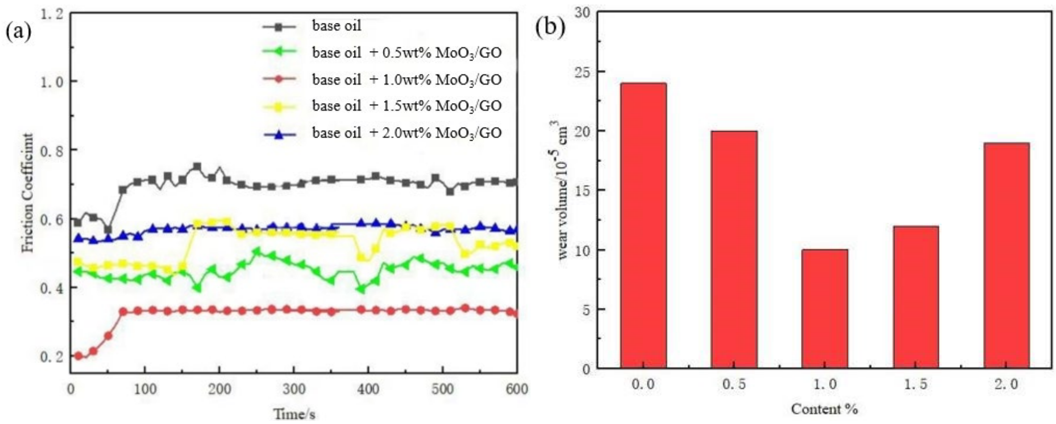

Fig. 5. (a) The changes of the real-time friction coefficient of MoO_3/GO additives with different concentration, and (b) the wear volume of additives with different concentration.

In order to compare the tribological properties of MoO_3/GO composite materials with MoO_3 and GO nanomaterials, comparative experiments were conducted under different loads and different speeds. Fig. 6a shows the average friction coefficient as a function of applied load when the additive concentration was 1 wt% and the tribotester was operated with a speed of 20 mm/s for 600 s. It can be seen from the figure that as the load increases, the average friction coefficient first decreases and then increases. The friction coefficient of MoO_3/GO composite also showed a decrease initially, but when the load increased to 65N, the friction coefficient began to increase. According to adhesive friction theory $\mu = A\tau/F$ (where μ is the friction coefficient, A is contact area, τ is the force per unit contact area and F is load), it can be observed that as the load increases, the contact area between the friction pairs also increases. However, the increase in contact area lags behind the increase in load, resulting in an inverse relationship between load and friction coefficient. However, as the load continues to increase, the surface wear of the steel plate increases, which leads to increased oxidation in the micro-areas on the contact surface, causing the friction coefficient to increase.

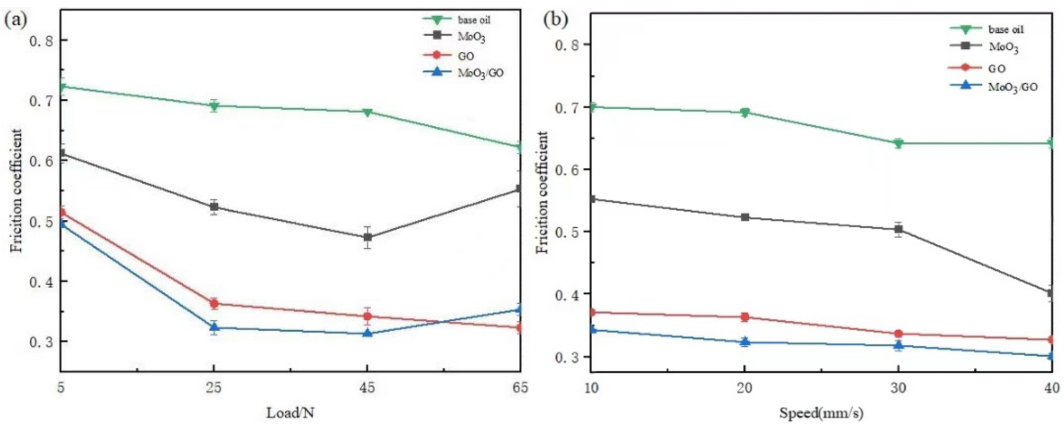

Fig. 6. The average friction coefficient change curve at different loads(a) and different speeds (b).

The variation of the average friction coefficient of the three kinds of different nanomaterials with the change of rotating speed is presented in Figure 6b. It can be observed that the addition of nanomaterials reduces the friction coefficient at different speeds to varying degrees compared with the base oil. Notably, molybdenum trioxide exhibits significant sensitivity to speed variations while GO shows minimal changes. In contrast, the composite material exhibits a relatively stable friction coefficient with a decreasing trend as the sliding speed increases. The reason for the above phenomenon is that the adsorption film formed by nano-molybdenum trioxide on the surface of the friction pair is potentially unstable and brittle, which can easily lead to its destruction, thereby causing the average friction coefficient to fluctuate within a certain range. On the contrary, graphene forms a relatively stable lubricating film on the surface of the friction pair, thereby producing a stable friction coefficient. The synergistic effect of molybdenum trioxide and GO makes the friction reduction effect of lubricating oil added with MoO_3/GO composite material better. As the speed increases, the friction coefficient decreases, and the friction and wear trend of the steel ball surface becomes stable. This observation shows that when used as an additive, the MoO_3/GO composite can form a film on the wear surface very quickly, thereby achieving the effect of reducing friction.

The SEM image in Fig. 7 illustrates the morphology of the disk surface after conducting friction experiments with varying concentrations of nano-additives. As depicted in Fig. 7a, when base oil is used as lubricant, the worn surface shows deep and irregular grooves and a large number of spalling pits, showing an irregular adhesive wear pattern, indicating that adhesive wear is the main wear mode. When MoO_3/GO nanocomposite was added to the lubricating oil, the morphology of the wear scars on the surface of the steel disc changed significantly, as shown in Fig. 7b, c, d and e. It is worth noting that when the addition concentration of nanocomposites is 0.5 wt%, the wear scars show fine and regular traces. In addition, Fig. 7c shows that adding 1 wt% MoO_3/GO can make the wear surface smoother and significantly reduce spalling pits, proving the excellent friction-reducing and anti-wear effects of MoO_3/GO as an additive. When the additive concentration is 2%, the wear marks and grooves on the surface of the friction pair increase, the grooves are thicker, and the surface structure is broken, as shown in Fig. 7e. This indicates that excessive addition of MoO_3/GO composite weakens its anti-wear function.

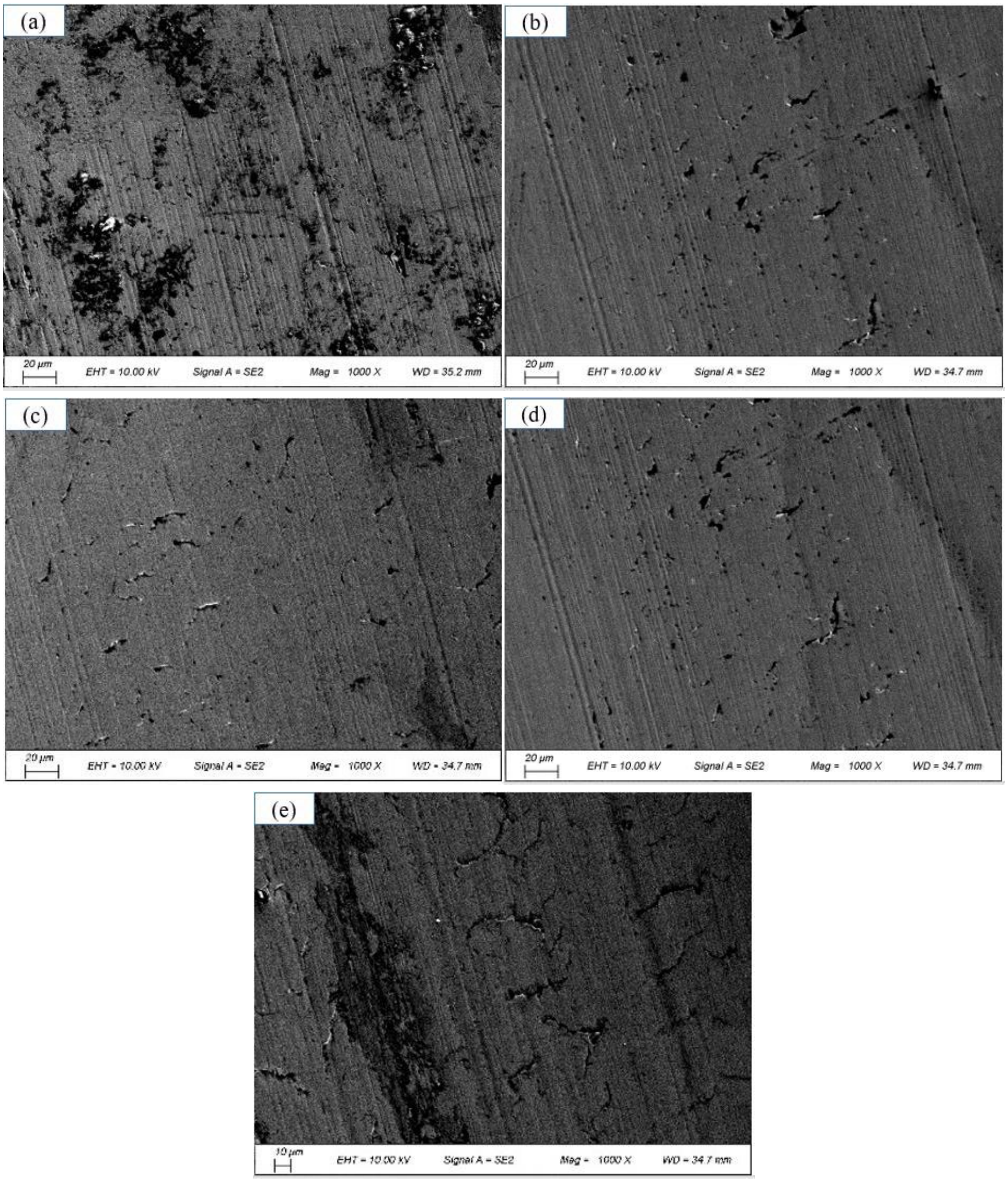

Fig. 7. SEM images of worn surface lubricated with pure base oil (a), base oil + 0.5 wt% MoO_3/GO (b), base oil + 1.0 wt% MoO_3/GO (c), base oil + 1.5 wt% MoO_3/GO (d) and base oil + 2.0 wt% MoO_3/GO (d)

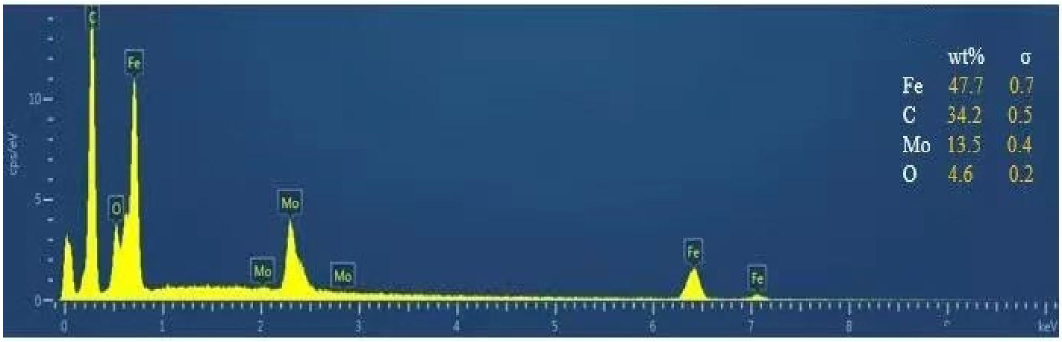

Fig. 8. EDS spectra of the wear surface lubricated with MoO_3/GO.

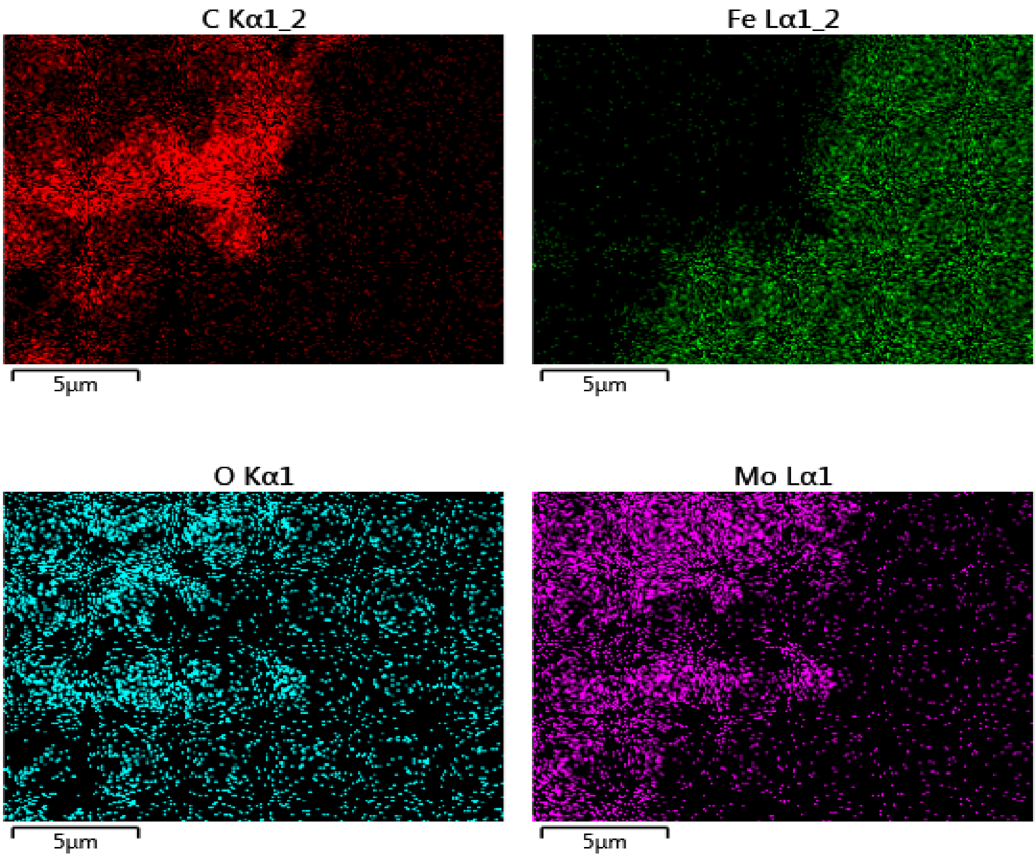

Fig. 9. Distribution of elements on worn surfaces.

The EDS spectrum and surface element distribution of the worn surface are shown in Fig. 8 and 9. It can be clearly seen from Fig. 9 that Fe, O, Mo and C elements are distributed on the surface of the steel plate. These elements can react to form oxides and molybdenum compounds that help form a lubricating film during friction. This phenomenon plays a vital role in reducing friction and wear.

3.3 MoO_3/GO lubrication mechanism analysis

The lubrication mechanism of MoO_3/GO is illustrated in Fig. 10. When the content is 0.5wt% (Fig. 10a), only a limited amount of nanomaterials can penetrate the friction surface, resulting in insignificant lubrication effect. On the contrary, when the content is 2.0wt% (Fig. 10c), the nanomaterials agglomerate in the friction area, forming a barrier that hinders the continuous supply of nanomaterials to the lubrication area[20]. Furthermore, it is postulated that nanomaterials capable of maintaining their rolling motion between the sphere and the disk exhibit continuous degradation of the frictional area during frictional contact. When the MoO_3/GO concentration is 1.0 wt%, the lubricating oil can effectively transport nanomaterials to the friction area with minimal agglomeration (Fig. 10b). Therefore, the optimal concentration of MoO_3/GO in lubricating oil is 1.0wt%.

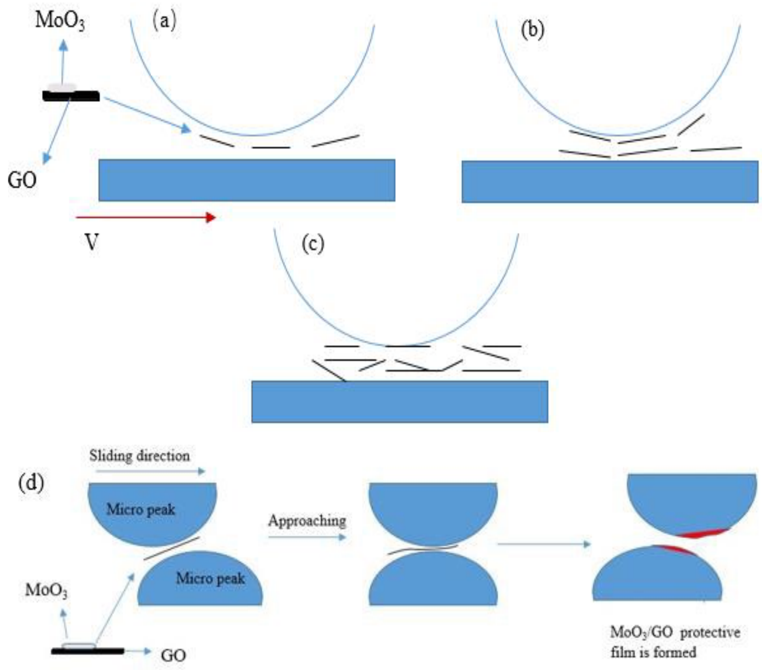

Fig. 10. The lubrication mechanism model of lubricants with (a) 0.5wt% MoO_3/GO, (b) 1wt% MoO_3 /GO, (c) 2wt% MoO_3/GO; and (d) model diagram of lubricating film formation process.

Based on SEM surface morphology and EDS element analysis, the lubrication mechanism model of MoO_3/GO composite as an additive was derived, as shown in Fig. 10d. In this model, MoO_3 is attached to the surface of graphene oxide, and the composite is dispersed in the lubricating oil in a sheet-like structure. Furthermore, the extremely thin thickness of MoO_3/GO composites facilitates their easy penetration into the sliding contact area. When the roughness peak of the first surface is close to the roughness peak of the second surface, MoO_3/GO is adsorbed on the contact surface in a flake state [21-23]. When the two opposite peaks of the ball and the disk come into contact, the friction pair cannot directly contact because there is a layer of MoO_3/GO on the friction surface. Although they may undergo edge deformation due to applied loads, wear on both surfaces is minimized under the protection of the composite material.

Based on the aforementioned experiments and analysis, it can be inferred that the wear mechanism of MoO_3/GO as an additive involves adhesive wear and corrosive wear. This is attributed to the fact that during relative motion between the friction pairs, GCr15 exhibits higher hardness compared to 45 steel, resulting in the formation of numerous grooves on their surfaces and consequently leading to adhesive wear. In addition, the plowing action generates fresh metal surfaces on the 45 steel plate surface, which react with the water present in the lubricant to produce loose iron oxides and hydroxides that intensify corrosion on the 45 steel plate surface. As a result, a detrimental cycle of increased friction and wear is formed. It is worth noting that the MoO_3/GO composite material is introduced into the lubricant, adsorbed or deposited on the friction contact surface, and penetrates into the friction pair interface to form an adsorption film. Due to the uniform loading of nano-MoO_3 onto the single-layer graphene sheet in MoO_3/GO, under the influence of frictional shear forces, weakened interlayer interactions within the composite material lead to separation and formation of an adsorption film. In addition, when the contact area is subjected to instantaneous high-temperature and high-pressure conditions, a tribochemical reaction will occur between MoO_3/GO and the worn surface, forming a chemical reaction film composed of C, Fe, O and Mo elements. Notably, GO exhibits excellent anti-wear properties in this composite as it can effectively fill scratches during friction while also exhibiting self-healing capabilities. The joint action of the adsorption film, tribochemical reaction film and nano-MoO_3 results in a significant reduction in friction coefficient and wear amount, thus enhancing the friction-reducing and anti-wear properties of the lubricating oil.

4. Conclusion

The MoO_3/GO composite materials were synthesized via a hydrothermal method, and MoO_3 was evenly distributed on the surface of graphene oxide. The addition of MoO_3/GO composite as an additive significantly improves the friction properties of the lubricant. It is worth noting that the average friction coefficient and wear volume of lubricating oil added with MoO_3/GO composite are 46% and 42% lower than those of the base oil, respectively. The MoO_3/GO composite materials are beneficial to the formation of lubricating films that resist adhesive wear and severe corrosion. The adsorption film formed by the MoO_3/GO composite material on the wear surface, combined with the chemical reaction film and self-healing MoO_3 nanoparticles, synergistically enhances the anti-wear and friction-reducing ability of the lubricating oil.

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