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Modifying the lubricating and tribological properties via introducing the oleic acid in CuS nanomaterials for vehicle

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ABSTRACT

Materials made from self-lubricating inorganic and organic composites have gained great attention due to advantages of the rust-resistance, light weight, low cost, and high compatibility. As a result, they have extensive applications in the friction and lubrication fields, typically for vehicle. With the help of the water bath and hydrothermal method, we have prepared the CuS nanomaterials with and without oleic acid modification. Various techniques, such as X-ray diffraction (XRD) spectra, transmission electron microscope (TEM), energy-dispersive X-ray spectroscopy (EDS) and vertical universal friction as well as wear testing, have been employed to analyze the structure information and characterize the related tribological properties of our CuS nanomaterials. Results show that the morphologies of the CuS nanomaterials are nanorods. Increasing the surface area and the concentration of CuS nanorod additives can significantly reduce the friction coefficient and wear rate of pins in both unmodified and oleic acid-modified CuS nanomaterials. More than that, we find that when compared to those without oleic acid modification, the oleic acid modification enable the CuS nanomaterials to exhibit higher anti-wear properties. The EDS analysis shows that there is still a uniform tribo-film in the surface of oleic acid-modified CuS nanomaterials, implying the prominent tribological performances of CuS nanorods additives. Our results indicate that the Oleic acid-modified CuS nanorods can be served as a new lubricating and tribological material for vehicle.

1. Introduction

Nowadays, nanomaterials, which can be served as the lubricating additives to enhance anti-wear properties, have attracted great attentions in the friction and lubrication fields [1–3], typically for vehicle. It has been known that not only the machine oil is one kind of the lubricating oil for lubricating the vehicle engine [1,4], but also it can effectively reduce the corrosion and vibration as well as the heating from the vehicle engine [1,5–7], which thus makes the vehicle engine maintain better. Due to the long-term and rapid friction from the vehicle engine, the practical inner temperature sometimes can be to 600 °C, which indicates that selecting suitable machine oil is extremely important for the vehicle engine to hold the desirable usage lifetime. Recently, the most effective methods to reduce the friction and wear that emerge in machine operation is to add the lubricating oil with nanoscale, because using the nano-additives as lubrication can increase the tribological behavior of lubricants. Up to now, nanolubricating additives, such as nano-sulfide [8], nano-oxide [9], nano-metal [10] and nano-borate [11,12], have been reported. Taking MoS_2 nanoparticles for example, Zhang et al. [13] found that adding 50 nm MoS_2 nanoparticles can give rise to excellent lubricating properties, and Hu et al. [14] further found that 1.5 wt% MoS_2 is the optimal content for achieving the best antifriction and anti-wear properties. In view of this, improving the exited lubricating oil properties is very important for extending the usage lifetime of the vehicle parts, and by using the nanomaterials with lubricating properties is a good choice. In addition, Yu et al. [15] found that the CuS nanowires can increase the PPS wear resistance, and Liu et al. [16] found that mixing the FeS nanoparticles into oil can also enhance the oil anti-wear properties. However, there are still many disadvantages in the existed lubricating oil, for example, the anti-wear property, the insolubility and poor stability of the nano-additives. All of these lead to great negative impact on the tribological properties for the vehicle parts.

Among the above-mentioned examples, CuS, due to the layer structure, can exhibit the excellent anti-wear properties, and the related tribological properties have been studied extensively. Liu et al. [17] studied the CuS tribological properties by varying mole ratios of oleic acid to copper sulfide, and found that the

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anti-wear properties of the base oil can be improved up to 50% when the mole ratio is 2:1. However, as can be seen, due to the lack of a direct contrast between pure and surface-modified CuS nanoparticle additives typically in the oil, the true CuS property as an additive is actually difficult to identify. Even some researchers have realized the importance of nano-additive size in wear properties, the related studies on the influence of size or surface area of CuS nanoparticles on wear properties are still extremely lacking. Therefore, these existing issues have limited greatly CuS nanoparticles as lubricating additives in base oil. All of these return to tell us that the wear property of CuS nanoparticle has seldom been noticed as an oil additive in the previous works, which therefore highlights the importance of the in-depht study of the CuS lubricating for industrial application.

Based on the above-mentioned content, here we synthesized the CuS nanorods with and without oleic acid modification by using the water bath and hydrothermal method. The lubricating and tribological properties of unmodified and oleic acid-modified CuS nanorods as an additive have been characterized and analyzed. All the results have indicated that the nanorod additives could be applied to lubricate the vehicle parts.

2. Experimental

2.1. Sample preparation

Our samples are synthesized according to the following steps. Firstly, 0.030 mol C_2H_5NS and 0.025 mol $Cu(CH_3COOH)_2{\cdot}H_2O$ were dissolved in a 150 mL flask with 75 mL water. Then, cupric acetate was added by drop into the thioacetamide solution by using the water bath, and the temperatures are controlled at 30 and 70 °C, respectively. The process needs 10 h stirring. After that, the mixed solution was transferred into two 100 mL Teflon-lined stainless steel autoclaves, and kept the temperature at 150 °C for 10 h to guarantee the complete solution reaction. With the temperature naturally cooling down to the room temperature, black precipitates could be obtained. After centrifuging, washing with distilled water and carefully drying at 80 °C for 8 h, we could obtain the targeted precipitates of CuS nanorods. The process of oleic acid modified CuS nanorods was similar to the unmodified CuS nanorods, except for the addition of 20 mL oleic acid.

2.2. Characterization

The crystal structure and phase purity of all above phosphors were identified by a Rigaku XD2-XRD diffractometer with Cu Kα radiation (λ = 1.5418 Å). The tube voltage, current and scanning step were 40 kV, 40 mA and 0.02°, respectively, and the XRD data were collected with the 2θ range from 25° to 60°. A transmission electron microscopy (TEM), which bases on a JEM 2100 apparatus with an acceleration voltage of 200 kV, was used to characterize the morphologies of unmodified and oleic acid modified CuS nanorods. The surface areas of the CuS nanorods, which were determined through the nitrogen adsorption data, were evaluated with a porosity analyzer, using using the Brunauer-Emmett-Teller technique on a BEL SORP max surface area. The tribological properties of unmodified and oleic acid modified CuS nanorods as lubricant additives were investigated by vertical universal friction and wear testing machine (MM-W1A). The images of pin surfaces after the friction and wear tests were observed with a MM-6 wide field microscope, and the element composition of worn pins surfaces was analyzed using a GENESIS energy dispersive spectroscopy with an acceleration voltage of 20 kV.

3. Results and discussion

3.1. Structural and morphology analysis

XRD patterns of CuS nanorods with and without oleic-acid modification are shown in Fig. 1(a) and Fig. 1(b). As can be seen, all the XRD peaks of unmodified and oleic acid-modified CuS nanorods are consistent with that of the data derived from the standard card of JCPDS No. 06-0464, indicating we have achieved the targeted hexagonal CuS products. Furthermore, the figure shows that increasing the preparation temperature can turn the XRD peaks to be narrower and the related intensity to be stronger. This is because with the increase of the temperature enables increasing the particle sizes of the two samples and, in the meanwhile, decreasing the particle surface area [1,17,18].

For our unmodified and oleic acid-modified CuS samples synthesized at 25 °C. We have measured their SEM image, as shown in Fig. 1(c-d). From the two figures, we can observe that the morphologies of the sample belong to nanorods. Modifying CuS nanorods with oleic acid can lead to a slight rougher surface, their average diameter and length are not changed significantly, still keeping at about ~10 nm and ~60 nm, respectively. Based on the SEM results, the surface areas of the unmodified CuS nanorods synthesized at 25 °C can be evaluated to ~23.895 m^2/g, as listed in Table 1. In addition, we found that increasing the preparation temperature can decrease the surface areas of the unmodified CuS samples, in which the surface areas that correspond to preparation at 50 and 160 °C are 21.034 and 14.689 m^2/g, respectively. However, since it is too viscous for the oleic acid-modified samples, the surface area variation similar to unmodified CuS nanorods can be observed with the increase of the temperature (see Table 1).

3.2. Tribological and friction surface performance analysis

After determining the structural and morphology of unmodified and oleic acid-modified CuS nanorods by using the XRD and SEM images, next we will show their friction and wear performances as the lubricating oil. The average friction coefficient of pins with different preparation temperatures of unmodified and oleic acid-modified CuS nanorods added into LP are shown in Fig. 2(a) and (b) as well as Table 1, respectively. These results have obviously shown us that the average coefficient of pins without CuS nanorods addition was 0.09, showing a slight higher than that with CuS nanorods addition. Increasing the preparation temperature from 25 °C to 160 °C enables slightly increasing the average friction coefficient of unmodified CuS nanorods from 0.0638 to 0.0696. In addition, the average friction coefficients between unmodified and oleic acid-modified CuS nanorods prepared at 50 °C and 160 °C are similar, but the average friction coefficient (~0.0345) has been reduced dramatically when compared with oleic acid-modified CuS nanorods prepared at 30 °C. That is to same, the increased anti-wear ability of the lubricating oil followed by a drastic reduction in average coefficient, which is due to the stable dispersion of surface-modified nanorods, appears (Table 2).

In Fig. 2(b) and Table 1, we can note that the wear rate of pins without adding CuS nanorods exhibits higher than that those with additives. The wear rate without nano-lubricants was 6.26×10^{-15} $m^3\,N^{-1}\,m^{-1}$, and the value decreases with increasing the surface areas of the nano-lubricants, namely, from $2.53 \times 10^{-16}\,m^3\,N^{-1}\,m^{-1}$ to $3.05 \times 10^{-17}\,m^3\,N^{-1}\,m^{-1}$ with oleic acid-modified CuS nanorods when the temperature is changed from 150 °C to 30 °C, and from $9.48 \times 10^{-16}\,m^3\,N^{-1}\,m^{-1}$ to $2.37 \times 10^{-16}\,m^3\,N^{-1}\,m^{-1}$ with unmodified CuS when the temperature is changed from 150 °C to 30 °C. These are because higher surface areas of