ARTICLE IN PRESS

Ceramics International (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Preparation and tribological properties of unmodified and oleic acid-modified CuS nanorods as lubricating oil additives

Lijuan Chen[a,*], Dingyi Zhu[b]

[a] Department of Safety Technology and Environmental Engineering, Fujian Chuanzheng Communications College, Fuzhou 350002, PR China
[b] School of Materials Science and Engineering, Fuzhou University, Fuzhou 350108, PR China

ARTICLE INFO

Keywords:
CuS nanorod
Tribological property
Lubricating oil additive
Anti-wear

ABSTRACT

Unmodified and oleic acid-modified CuS nanorods were prepared by water bath and hydrothermal method. The prepared CuS nanorods were characterized by X-ray diffraction and transmission electron microscope. The tribological properties of both types of CuS nanorods as additives in liquid paraffin (LP) were investigated using a vertical universal friction and wear testing machine. The addition of unmodified and oleic acid-modified CuS nanorods was found to significantly reduce the friction coefficient and wear rate of pins by increasing the surface area and addition concentration of CuS nanorod additives. The addition of oleic acid-modified CuS nanorod showed higher anti-wear properties than those of unmodified CuS nanorods. The prominent tribological performances of CuS nanorods additives were attributed to the formation of complete and uniform tribo-film , which is confirmed by the EDS analyses of tested worn surfaces of pins.

1. Introduction

Nanoparticles as lubricating additives to enhance anti-wear properties have piqued the interest of researchers. The addition of lubrication is an effective method to reduce friction and wear, which are inevitable phenomena in machine operation. Adding nano-additives into lubrication can also increase the tribological behavior of lubricants. Nano-lubricating additives include nano-sulfide, nano-oxide, nano-metal, and nano-borate [1–5]. The nano-sulfide's weak layer force during wear and friction contributes to its excellent lubricating properties. The layer structure of nano-sulfide includes MoS_2, FeS, and WS_2 [6–10]. Zhang et al. found that the addition of 50 nm MoS_2 nanoparticles resulted in excellent lubricating properties [6]. Hu et al. found that MoS_2 with percent of 1.5 wt% showed the best antifriction and anti-wear properties and nano-slice MoS_2 with percent of 1.0% showed the best properties [7]. Paskvale et al. found that the addition of MoS_2 nanotubes leads to a significant reduction in the friction and an improvement in the wear behavior compared to pure PAO oil [8]. Yu et al. found that CuS as the filler increased the wear resistance of PPS [9]. Liu et al. found that FeS particles mixed into oil can also enhance the anti-wear properties of the oil [10]. However, the insolubility and poor stability of the nano-additives may limit their application as lubricating additives.

The preparation of surface-modified nanoparticles can solve the above- mentioned problem regarding the stable dispersion of additives. Improved tribological properties can be achieved by many surface-modified nanoparticles, such as surface-modified multi-walled carbon nanotubes, zinc borate ultrafine powder, and magnetic silica nano-composite [11–13], all of which are enhanced by surface- modified additives. For example, Zhao et al. studied the performance of hexadecyltrimethoxysilane-modified zinc borate as a lubricant additive in liquid paraffin (LP), and found it resulted in a small conglomerate size, good stability in the organic solvent, and sound anti-wear property [12]. CuS should display excellent anti-wear properties because of its layer structure. However, its wear property as an oil additive has seldom been studied. Kang et al. studied the tribological properties of varying mole ratios of oleic acid to CuS and found that when the mole ratio of oleic acid to copper sulfide is 2:1, the lubricating oil additives can improve the anti-wear properties of the base oil by about 50% [14]. However, without a direct contrast of pure and surface-modified CuS nanoparticle additives in the oil, the true property of CuS as an additive in LP cannot be identified. Whether CuS nanoparticles alone or a surface modification agent improves their wear properties remains unclear. Furthermore, even with the acknowledged importance of nano-additive size in wear properties, studies on the influence of size or surface area of CuS nanoparticles on wear properties are still lacking. These problems may limit the practical application of CuS nanoparticles as lubricating additives in base oil. Therefore, a study on pure and oleic acid-modified CuS nanoparticle additives and the influence of their surface areas on wear properties is imminent for a

* Corresponding author.
E-mail address: clj790115@163.com (L. Chen).

http://dx.doi.org/10.1016/j.ceramint.2016.12.066
Received 1 November 2016; Received in revised form 11 December 2016; Accepted 12 December 2016

proper investigation of the lubrication mechanism of additives and their industrial application.

In this study, unmodified and oleic acid-modified CuS nanorods were synthesized by water bath and hydrothermal methods. The wear properties of LP with unmodified and oleic acid-modified CuS nanorod additives were investigated. A protective tribo-film was formed during the wear process, which may be the reason for the enhanced anti-wear performance. The nanorod additives could be applied to lubricate fixed hydraulic equipment indoors.

2. Materials and experimental apparatus

2.1. Materials

C_2H_5NS, Span-80, $Cu(CH_3COOH)_2{\cdot}H_2O$, and LP were of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. Analytically pure LP was used as the lubricant base oil.

2.2. Sample preparation and characterization

First, 0.015 mol C_2H_5NS and 0.01 mol $Cu(CH_3COOH)_2{\cdot}H_2O$ were carefully dissolved in 75 mL water at room temperature. Cupric acetate was then added drop by drop into the thioacetamide solution at different water bath temperatures (30 and 70 °C) while stirring for 10 h. The mixed solution was transferred into two 100 mL-capacity Teflon-lined stainless steel autoclaves to react at 150 °C for 10 h. After the solution was naturally cooled to room temperature, the black precipitate was centrifuged and sufficiently washed with distilled water. The resulting samples were air-dried at 80 °C for 8 h. The oleic acid-modified samples were prepared using a similar process as the unmodified samples, except that 10 mL oleic acid was added into the solution with stirring.

Sample structures were examined through powder X-ray diffraction (XRD) using a D8 Focus diffractometer with monochromatized CuK_α radiation (λ=0.15418 nm). Morphologies of the as-obtained products were observed through transmission electron microscopy (TEM) using a JEM 2100 apparatus with an acceleration voltage of 200 kV. A porosity analyzer was used to determine the specific surface areas of the CuS nanorods from nitrogen adsorption data at liquid nitrogen temperature using the Brunauer–Emmett–Teller technique on a BEL SORP max surface area.

2.3. Wear tests

The tribological properties of nanorods as lubricant additives were investigated by vertical universal friction and wear testing machine (MM-W1A). Before and after each test, the pins and discs were cleaned with acetone in an ultrasonic water bath for 5 min to eliminate potential impurities and then dried. The lost mass of the pins was weighed by balance with a sensibility of 0.0001g. Unmodified and oleic acid-modified CuS nanorods of varying surface areas and with an addition percent of 1 wt% were added carefully into 2 mL LP with the 1 wt% dispersing agent Span-80. The solution was then dispersed ultrasonically for 0.5 h to obtain a well-dispersed nano-lubricant. All the tests were carried out with 300 N loads, in room temperature, a testing period of 60 min with a sliding speed of 300 r/min and five drops of the above nano-lubricant on the disc, this environment of testing could be applied for lubrication of fixed hydraulic equipment indoor. The disc is composed of bearing steel with a hardness of 44-55HRC. The pins used in the test were made of pig iron with a hardness of 25–30 HRC, diameter of 4.78 mm, and height of 12.56 mm. The selection of pig iron is just because of its low hardness, which could be shown obvious experimental result. The same process was done with nano-lubricants with addition percents of 0 wt%, 0.5 wt%, 1.0 wt%, and 2.0 wt%. The results of the friction and wear tests were calculated using the friction coefficient and wear rate. The images of pin surfaces

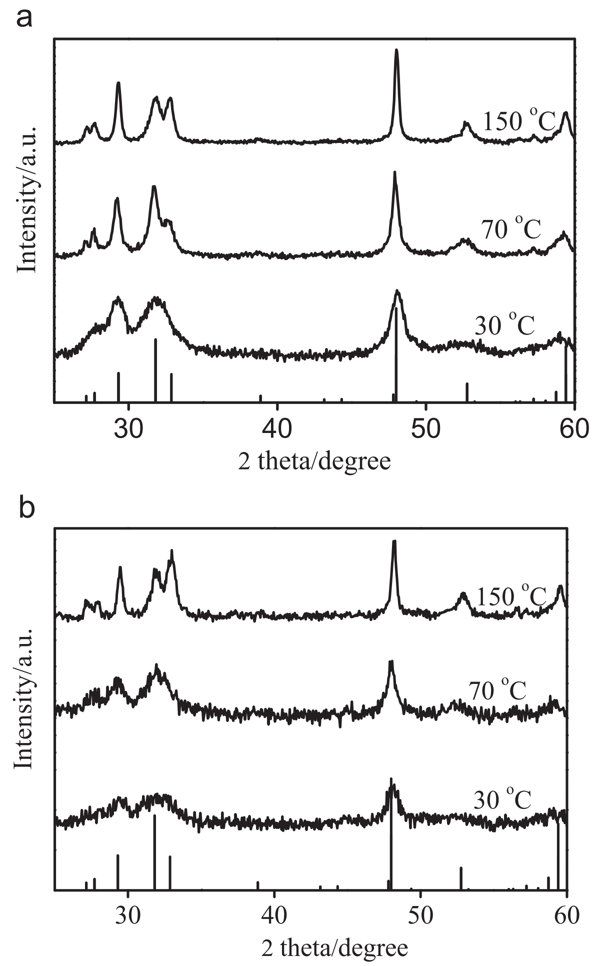

Fig. 1. XRD patterns of (a) unmodified CuS and (b) oleic acid modified CuS nanorods. Vertical bars represent the standard diffraction data of CuS nanorods from JCPDS file (no. 06-0464).

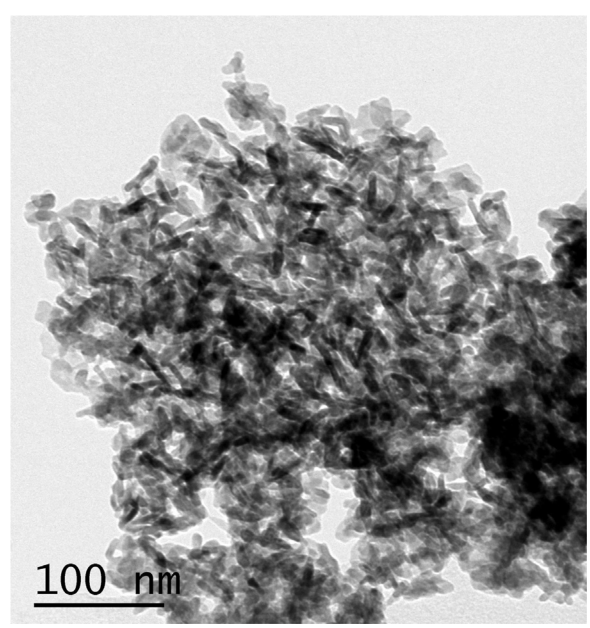

Fig. 2. TEM images of unmodified CuS nanorod prepared at 30 °C.