Wear 288 (2012) 9–16

Contents lists available at SciVerse ScienceDirect

Wear

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

Fundamental understanding of the tribological and thermal behavior of Ag–MoS_2 nanoparticle-based multi-component lubricating system

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ARTICLE INFO

Article history:
Received 12 October 2011
Received in revised form 13 March 2012
Accepted 21 March 2012
Available online 30 March 2012

Keywords:
Solid lubricants
Lubricant additives
Boundary lubrication
Nanotribology
Tribochemistry
High temperature

ABSTRACT

The objective of this study is to investigate the tribological and thermal properties of the recently developed Ag–MoS_2 nanoparticle-based multi-component lubricating system. To obtain greater tribofilm durability and to enhance the tribological and thermal properties of MoS_2, a chemo-mechanical processing method has been developed for the synthesis of composite silver nanoparticles (Ag NPs) incorporated into MoS_2 nanoparticles (nMoS_2). In order to characterize and investigate thermal and tribological behavior of the Ag–MoS_2 hybrid system, four different Ag compositions were studied, ranging from 2 to 25 wt. % in MoS_2. Different characterization techniques have been used to examine structural properties, silver content, particle size, and particle size distribution. The characterization results showed that the Ag NPs were successfully embedded into nMoS_2 with particle sizes lower than 300 nm for 90% of agglomerated particles and 100 nm for most of de-agglomerated particles with no phase change of the system. The increase of internal strain of nMoS_2 from the order of 0.002 to 0.02 was confirmed by XRD after the successful embedding of Ag NPs into nMoS_2. In addition, the chemical and thermal analysis showed that silver molybdate was formed at temperatures above 450 °C, which demonstrates that this multicomponent system should be very effective for high temperature applications. The tribological tests revealed that nMoS_2 – 2 wt. % Ag results in 15–20% reduction in friction under boundary lubricated sliding conditions and 30–37% reduction in wear. Therefore, the addition of Ag nanoparticles at an optimum concentration can significantly enhance the thermal and tribological performance of the developed Ag–MoS_2 hybrid system.

1. Introduction

Many of the current lubricants that are in use today contain numerous chemical additives in order to improve, their thermal, physical and tribological properties. Although some of these additives can improve the tribological properties of sliding surfaces by substantially lowering friction and wear, they may also have some negative effects. For example, many engine oils use zinc dithiophosphate (ZDDP) or other phosphorus and sulfur-bearing compounds to reduce friction and wear. These compounds can improve the lubricity and reduce wear and scuffing problems in engines, but they can also adversely impact the performance of after treatment devices and catalytic converters [1]. In the past few years, significant progress has been made in the synthesis of advanced nanolubricants [2–9]. Some previous studies focused on synthesis and testing of several single component nanomaterials like Ag, Cu, Ni, MoS_2, WS_2, etc. [10–14] and showed that the nanoparticles of these materials can offer various benefits like friction reduction, wear resistance, high fuel efficiency, energy savings, and low harmful emissions. Especially, soft metal nanoparticles, such as copper nanoparticles and silver nanoparticles, showed significant friction reduction and wear resistance when they are added at a small concentration (less than 1 wt.%) [10,11]. Also, addition of 1 wt.% of metal dichalcogenides nanoparticles, like MoS_2 nanoparticles and WS_2 nanoparticles exhibited excellent tribological properties under different tribological regimes (hydrodynamics, mixed, and boundary lubrication) [13,14]. However, in spite of extensive research and development efforts through the years, there still has been no single designed solid lubricant additive which can provide both friction reduction and wear resistance over broad application conditions and temperatures [15].

Molybdenum disulfide (MoS_2), an important solid lubricant with excellent friction and wear properties under inert or vacuum environments, has been widely studied because of its unique

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0043-1648/$ – see front matter
http://dx.doi.org/10.1016/j.wear.2012.03.003

lamellar structure which enables low shear strength and hence low friction. However, its short life in humid environment and poor performance at high temperatures strongly limit its applications due to the formation of SO_2 and H_2S by reacting with water and formation of MoO_2 and MoO_3 by oxidation at high temperature [16,17]. To address these limitations of MoS_2 nanoparticles, a novel design and synthesis of nanoparticle based multicomponent architecture rather than single component design has been proposed in this study and the thermal and tribological performance of the multicomponent system has been studied. Silver (Ag) is a soft metal which exhibits low shear strength and has good embeddability allowing Ag nanoparticles to embed wear particles, such as failed solid lubricant particles and debris from work piece, into a softer lining [16]. Additionally, silver can form silver molybdate with molybdenum disulfide at higher temperature (above 350 °C), which has already been demonstrated as a good self-lubricating material for high temperature applications [18]. Based on the extensive literature survey on Ag and MoS_2 based nanolubricants and their tribological properties, it is expected that the addition of Ag NPs to MoS_2 nanoparticles can exhibit better tribological performance, especially at the high temperature applications. In this regard, the present study has been designed to integrate Ag nanoparticles into MoS_2 nanoparticles in order to create Ag–MoS_2 nanoparticle-based multicomponent system. In addition to the synthesis and characterization of the Ag–MoS_2 multi-component system, the chemical, structural, thermal, and tribological properties of this multi-component nanoparticle-based system have been studied extensively.

2. Experimental procedure

In order to develop the Ag–MoS_2 multi-component system, Ag nanoparticles (Aldrich, 99% pure, average particle size below 100 nm) of three different compositions (2, 5, and 10 wt.%) were integrated into MoS_2 particles (Alfa Aesar, 98% pure, 3–5 μm average particle size) by chemo-mechanical processing in air at room temperature. This top-down material processing procedure can create uniform size distribution by effectively mixing and crushing the source materials. After the mechanical processing, to minimize the agglomeration of mechanical processed particles [8], chemo-mechanical hybrid processing was performed using mixtures of above samples with MoDTP (RheinChemie) and lecithin (Alcolec® S, American lecithin Company) at 2:1:1 weight ratio at room temperature. A constant ball-to-powder ratio of 2:1 was selected in the chemo-mechanical processing [8]. During the chemo-mechanical processing, hardened stainless steel vials containing powder and hardened stainless steel balls were moved in three orthogonal directions to assure homogeneous processing. It moves very rapidly developing extremely high G forces to ensure the materials have been ground properly and to enhance the bonding among various materials in the vial. Vials and balls were cleaned using standard laboratory cleaning agents starting with soft soap followed by clean water, isopropanol, acetone and sonication steps. After above steps, samples were stored in controlled desiccators for characterization and further analyses.

After preparation, the samples were analyzed using particle size analyzer (Horiba Instruments LA950, 0.01–3000 μm) to obtain information about the size distribution of the particles. The morphology and structure of the multi-component system were analyzed by high resolution transmission microscopy (FEI *Titan* 80–300, operating voltage: 300 kV). In order to study the structure, stress–strain, and grain size of the samples, X-ray diffraction (Philips PW-3020 using Cu-Kα radiation with current of 30 mA and voltage 45 kV) analysis was used. Finally, the thermal properties were explored using TGA and DSC (Netzsch STA-409, up to 1500 °C) systems.

In order to study the tribological behavior of the Ag–MoS_2 hybrid system, five samples were prepared as shown in Table 1. The first sample was pure formulated oil which is composed of 25 cst 75W-140 Gear oil (Caterpillar) and PAO 8, 25, and 40 with 8 cst, 25 cst, and 40 cst (Chevron Philips). The following samples were prepared by adding chemo-mechanical processed MoS_2, 2% Ag–MoS_2, 5% Ag–MoS_2, or 10% Ag–MoS_2 additive to formulated oil at concentrations of 2% by weight. In order to ensure homogeneous dispersion, every sample was followed by physical agitation and sonication for 10 min after mixing with formulated oil. Tribological performance (coefficient of friction-COF and wear scar diameter-WSD) of all the samples was studied using a pin-on-disk tribometer (CSM-Instruments) and optical microscope (NIKON EPIPHOT 200) at room temperature (humidity: 40% ±5% RH). A load of 5-newton was used, and the wear track diameter was 10 mm. Trials were run at speeds varying from 0.13 to 16 cm/s in order to observe the performance of the lubricants under the boundary, mixed, and hydrodynamic regimes of the Stribeck curve. The tests began at 16 cm/s for 5 min and then ran for 5-min intervals at 12, 10, 8, 4, 2, 1, 0.5, 0.25, and 0.13 cm/s. The trail then went back to 0.25 cm/s for 5 min and followed the same pattern of 5-min intervals back to 16 cm/s. The contact surfaces used in the tribometer were a 52100 steel ball and a 52100 steel disk (R_c = 66). The ball had a radius of curvature of 6.35 mm. A bench-top circular wet sander was used to polish the 52100 steel disks with P2400 SiC paper. To decrease contact pressure, a standardized flattening procedure was developed to increase the radius of curvature of the ball to approximately 30–40 mm.

3. Results and discussion

3.1. Characterization

3.1.1. Analysis of size, shape, chemical, and crystal structure

As can be seen from the TEM image in Fig. 1a, the Ag nanoparticles have average particle size of about 100 nm and lower but they also show some tendency to agglomerate. As shown in Fig. 1b, the EDX analysis of the particles shown in Fig. 1a confirms that the nanoparticles in TEM image are Ag NPs. Fig. 2a shows TEM image of 2% Ag–MoS_2 sample after mechanical processing, which indicates there is obvious agglomeration between the nanoparticles. The EDX analysis of the entire TEM image is presented in Fig. 2b. Although, Ag peaks were observed in EDX graph with very lower counts (Fig. 2b), no separate Ag nanoparticles were directly observed inside and outside of MoS_2 nanoparticles in the TEM image (Fig. 2a). Therefore, it was believed that all Ag nanoparticles were integrated into MoS_2 nanoparticles. Moreover, it was demonstrated by elemental mapping as shown in Fig. 3 that silver nanoparticles (as shown by green color Fig. 3d) were well-dispersed in nMoS_2 after chemo-mechanical processing. The TEM image, electron diffraction patterns, and EDX spectrum results of 10% Ag–MoS_2 sample, as shown in Fig. 4a–c, respectively, demonstrate that silver nanoparticles were partly embedded into MoS_2 nanoparticles or absorbed by the surface of MoS_2 nanoparticles after chemo-mechanical processing, and the MoS_2 still maintained lamellar structure. In addition, the TEM images and diffraction patterns also revealed that no structural changes of MoS_2 occurred after incorporation of Ag NPs, which not only ensures the good lubricity (lamellar structure) of the hybrid system but also an indication of good wear resistance (dispersion strengthening of Ag NPs). However, as can be seen from Fig. 4a, at higher concentration of Ag–MoS_2 samples, part of Ag nanoparticles was not integrated into MoS_2 properly and was distributed outside of MoS_2 nanoparticles. In addition, Ag