

Comparison of Tribological Performance of WS₂ Nanoparticles, Microparticles and Mixtures Thereof

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ABSTRACT

Tribological performance of tungsten sulfide (WS₂) nanoparticles, microparticles and mixtures of the two were investigated. Previous research showed that friction and wear reduction can be achieved with nanoparticles. Often these improvements were mutually exclusive, or achieved under special conditions (high temperature, high vacuum) or with hard-to-synthesize inorganic-fullerene WS₂ nanoparticles. This study aimed at investigating the friction and wear reduction of WS₂ of nanoparticles and microparticles that can be synthesized in bulk and/or purchased off the shelf. Mixtures of WS₂ nanoparticles and microparticles were also tested to see if a combination of reduced friction and wear would be achieved. The effect of the mixing process on the morphology of the particles was also reported. The microparticles showed the largest reduction in coefficient of friction while the nanoparticles showed the largest wear scar area reduction. Mixtures of nanoparticles and microparticles did not provide the desired combination of significant friction and wear reductions.

CITATION: Daly Flynn, K., Harta, I., and Schall, J., "Comparison of Tribological Performance of WS₂ Nanoparticles, Microparticles and Mixtures Thereof," *SAE Int. J. Fuels Lubr.* 7(2):2014, doi:10.4271/2014-01-0949.

INTRODUCTION

Solid tungsten disulfide (WS₂) and molybdenum disulfide (MoS₂) thin films and powders show remarkable friction reducing properties. They are often used in high performance lubrication applications such as automotive racing and space travel [1]. The coefficient of friction (COF) of these compounds has been reported as low as 0.022 for WS₂ (in N₂) [2] and 0.002 for MoS₂ in ultra-high vacuum [3]. The proposed mechanism for this behavior is related to its graphite-like structure. The system crystallizes in a hexagonal structure of 2H platelets [4]. The bonding within one crystallographic direction is strong, but adjacent layers are bond with van der Waals forces. This weaker bonding facilitates slip between the planes leading to friction reduction. WS₂ and MoS₂ have also been synthesized in an inorganic-fullerene structure that shows large friction reduction [5]. The particles synthesize into round particles with spherical layers of atoms. The mechanism for friction reduction is that the round particles reduce friction by rolling between two surfaces and by shedding layers as necessary to further improve the tribological properties.

Another phenomenon that has been observed with MoS₂ and more prominently with WS₂ lubricants is a self-healing effect. Initially, the wear track shows the expected degree of wear upon the application of force in the sliding process, but after continued testing, the wear scar and pitting fill in such that the wear is less than before. This has been confirmed with SEM pictures [6, 7, and 8].

However, application as solid lubricants is limited. WS₂ and MoS₂ solid lubricants can be expensive and operate at their best in low oxygen environments (vacuum or N₂) making them impractical for standard usage. Researchers have added WS₂ and MoS₂ microparticles and nanoparticles to lubricating fluids in an attempt to retain the friction reduction properties while creating an air-stable lubricant and reducing the amount of nanoparticles needed [3,4,6,7,8,9,10,11,12].

X. Hu studied the effect of particle size of MoS₂ on tribological performance [7]. Solutions of 1% particles in liquid paraffin of varying ratios of MoS₂ nanoparticles to microparticles were compared. Both nanoparticles and microparticles were observed to reduce friction and wear. However, mixtures of showed a synergistic effect and lowered friction and wear to greater degree than either component alone. Because the structure of MoS₂ and WS₂ are similar, the same synergistic effect might be observed for WS₂ and deserves investigation.

The goal of this paper is to investigate and compare the tribological effect of WS₂ nanoparticles and microparticles in oil. In addition, mixtures of the two will be investigated to see whether, like MoS₂, the combination of micro and nanoparticles leads to greater improvement. The performance will be judged by COF and wear scar area reduction.

EXPERIMENTAL

Samples for analysis were prepared by mixing WS₂ nanoparticles (40-80 nm purchased from US Research Nanomaterials), WS₂ microparticles (0.8 μm purchased from SkySpring Nanomaterials) and combinations thereof with a stabilizer in lubricating oil. The stabilizer to particle weight ratio was 1:1. The stabilizer consisted of a 1:10 ratio of polyisobutenyl succinic anhydride and isostearic acid. The base oil was an API Group III oil. Samples were made in the following concentrations by weight: nanoparticle - 1%, 2%, 3%; microparticle - 0.5%, 1%, 2%, and 3%. For the mixtures of nanoparticles and microparticles, the WS₂ was added with a total of 3% by weight in the following ratios: [20% nano: 80% micro]; [40% nano: 60% micro]; [60% nano: 40% micro]; [80% nano: 20% micro]. All oil-particle mixtures were sonicated for 25 minutes in an ultrasonic bath then for 8 minutes at 200W with an Omni Sonic Ruptor 400 to achieve a homogeneous mixture. This mixing protocol was based on previous experience [13] and the work of Hwang *et al* [14]. Samples were used immediately after sonicating to avoid suspension separation.

Friction properties were measured on a CETR UMT-3 Ball-on-disc Test System on 1040 steel plates with 52100 steel balls with 7.94 mm diameter. The hardness of the steel plates and ball were found to be 82.6 HRB and 63.5 HRC, respectively. The surface of each steel plate was hand polished which resulted in an average surface roughness Ra value of 126 nm. The roughness of a typical ball bearing is 50-100 nm. Experimental conditions were T=21.8°C, Force = 8.9 N, angular velocity = 55 rpm, time = 30 min, sampling rate = 100 points per second. Wear on the steel plates was measured using WYKO NT1000 Optical Profiler. Two to three measurements per experiment were collected at locations 90° and 180° apart. No wear was evident in the steel ball.

RESULTS

Stability

As mentioned in the methods section, the fluids were used immediately after mixing to limit any effects related to fluid stability. However, because of the importance of stability on the real-world application of nanofluids fluid stability and particle morphology will briefly be discussed. Figure 1 shows scanning electron micrographs of the as received particles.

Both nano and micro sized particles exhibit significant agglomeration, although the nature of the agglomerates appears different for the two particle types. The nanoparticles tend to be agglomerated into spherical balls 1-5 μm in diameter. Some large thin flakes (~10 μm in diameter) are clearly evident in the images of the supposed nanoparticles. The spherical agglomerates appear to be comprised of many small flakes of WS₂, see figure 2. The agglomerates in the micro-sized particle sample appear to consist of loose clusters of flakes. The average microparticle size appears to be

consistent with the manufacturer's specification. In both the nano and micro particle samples, hexagonal shaped flakes are observed, which is consistent with the molybdenite crystal structure of WS₂.

The purpose of sonication during mixing is to break up the agglomerates that appear in the as received particles. To investigate the effectiveness of sonication, a few drops of both 1% by weight of nanoparticles and microparticles in oil were placed on the edge of a clear watch glass immediately after mixing, see Figure 3. The nanoparticles appear to have much better dispersion in the fluid. Flocculated agglomerates are clearly visible in the droplets containing microparticles.

To investigate the effect of sonication on the morphology of the particles, the watch glass was then placed in a furnace and held just above the flash point of the oil (245°C) for one hour to evaporate off the oil. Particles from near the edge of the watch glass were then removed using conducting carbon tape for examination in the scanning electron microscope.

Representative samples of both micro and nanoparticles are shown in Figure 4.

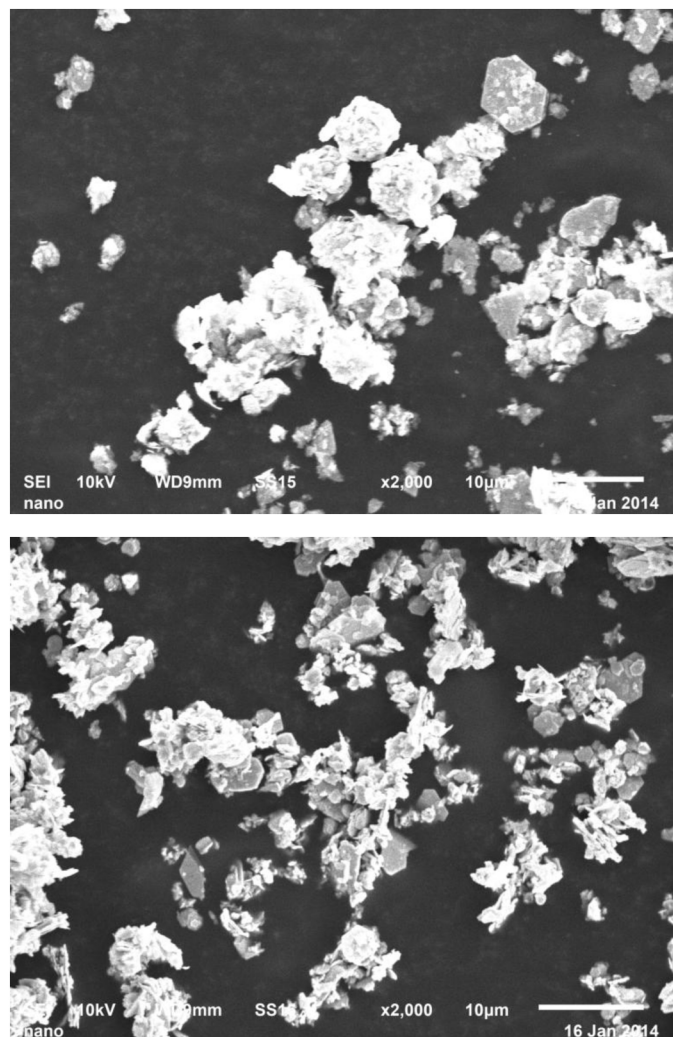


Figure 1. Representative SEM micrographs of as received nanoparticles (top) and microparticles (bottom).

The nanoparticles appear to be well dispersed and spherical agglomerates like the one shown in [Figure 2](#) are less frequently observed. Large numbers of particles with diameters on the order of $0.1\ \mu\text{m}$ are readily observed at high magnification, see [Figure 5](#). Contrary to the manufacturer's specified particle size ranging from 40-80 nm, flakes on the order of a few μm are also present, which is consistent with the particles observed prior to sonication ([Figure 1](#), top). The majority of the microparticles appear in large flocculated agglomerates like the one shown in [Figure 4](#) (bottom). The particles appear as large jagged flakes often with hexagonal structure.

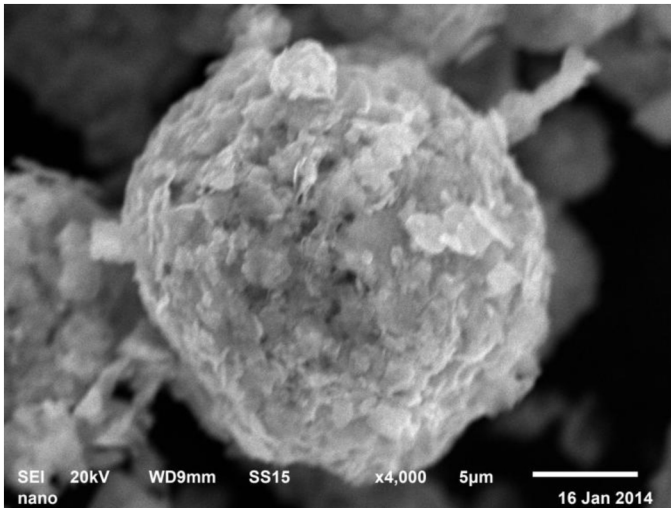


Figure 2. SEM image of a spherical agglomerate of nanoparticles.



Figure 3. Droplets of 1% by weight nanoparticles (left) and microparticles (right) in oil.

Stability of the solutions was qualitatively investigated by observing the rate of settling of particles in the sample vials. While a small number of larger agglomerates appear to settle

rapidly, both nano and micro solutions appear to remain stable for several hours (and certainly over the duration of the friction tests). All samples settled out after a few days of resting.

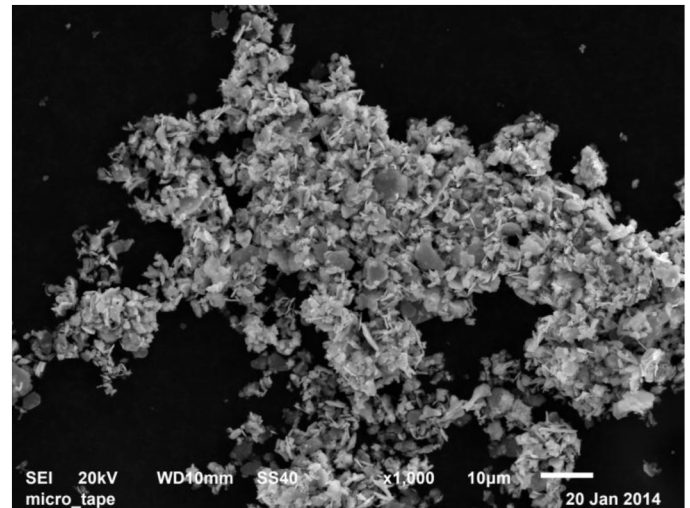
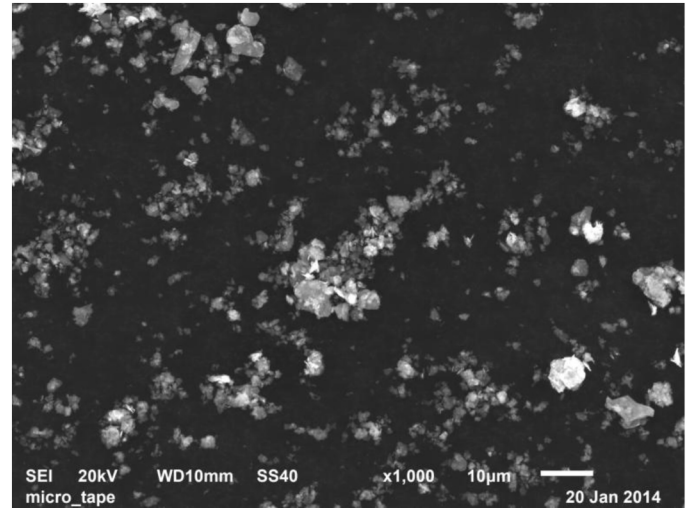


Figure 4. Representative SEM micrographs of nano (top) and micro (bottom) particles after sonication and evaporation of oil.

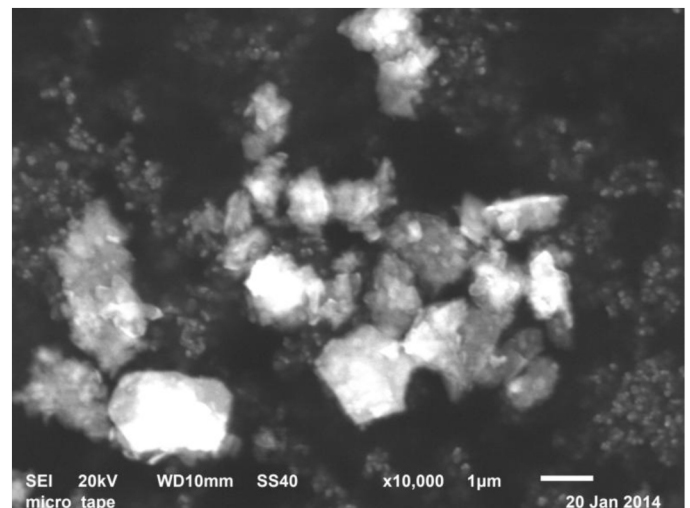


Figure 5. High magnification image of nanoparticles after dispersion and evaporation of oil. Small submicron sized particles are present amongst some larger flake-like particles.