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Operando formation of an ultra-low friction boundary film from synthetic magnesium silicon hydroxide additive

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ABSTRACT

The paper reports the operando and self-healing formation of DLC films at sliding contact surfaces by the addition of synthetic magnesium silicon hydroxide (MSH) nanoparticles to base oil. The formation of such films leads to a reduction of the coefficient of friction by nearly an order of magnitude and substantially reduces wear losses. The ultralow friction layer characterized by transmission electron microscope (TEM), electron energy loss spectroscopy (EELS), and Raman spectroscopy consists of amorphous DLC containing SiO_x that forms in a continuous and self-repairing manner during operation. This environmentally benign and simple approach offers promise for significant advances in lubrication and reduced energy losses in engines and other mechanical systems.

1. Introduction

A variety of approaches are being explored to reduce friction losses including new low-friction materials [1,2], coatings [3], nanolubrication additives [4–8], ionic liquids [9], charged polymer [10,11] and various low-viscosity base oils. Among these, diamond-like carbon (DLC) coatings have made their way into many industrial applications including hard disk drives, razor blades, engine parts and cutting tools [12]. The term DLC encompasses an array of amorphous carbon coatings and carbon-based nano-structured and nano-composite films [13]. Synthesis of DLC films for industrial applications generally involves plasma-based physical vapor deposition and chemical vapor deposition methods that are expensive and slow (it takes several hours to produce DLC films a few micrometers thick) [14]. Due to their limited thickness, the lifetime of DLC films is finite, and under severe loading situations such films are prone to delamination due to inadequate adhesion or substrate deformation [14]. Clearly it would be highly desirable to produce such DLC films at sliding contact interfaces in a continuous and self-healing manner. In this paper, we describe a novel lubrication approach that leads to in situ and operando formation of such films directly on the contact points where high lubricity and protection against wear are needed. This approach involves the use of a hydrocarbon base oil, such as a pure paraffinic oil, small amounts of MSH nanoparticles and some Ni catalysts.

Base oils used for lubrication provide only moderate protection without additives or some additional protective film on the sliding surfaces. Lubricant additives such as molybdenum dithiocarbamate (MoDTC) and zinc dithiophosphate (ZDDP) have been around for more than 50 years and still are the most important anti-friction and anti-wear additives [15]. MoDTC and ZDDP form slick, highly protective films on rubbing surfaces, but they can poison catalysts and cause environmental pollution [16]. As an alternative to ZDDP or MoDTC additions, addition of carbon nanomaterials such as nano-onions, -tubes or –spheres in colloidal dispersion to carrier oils to form carbon-rich tribofilms on sliding surfaces has been explored. These studies have shown that friction can be substantially reduced and that wear can be highly minimized with the formation of such tribofilms [12]. However, there have been very few attempts to extract similar tribofilms directly from the lubricating oils using catalytically active nanoparticles like those used in this study. Our innovative approach involves the operando formation of carbonaceous coatings by extracting carbon catalytically from the long chain molecules of the hydrocarbon-based carrier oil. This approach is very desirable since it does not rely on the repeated use of expensive, difficult-to-disperse carbon

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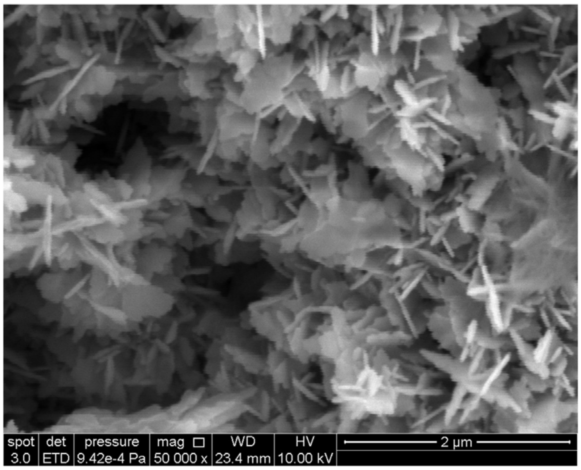

Fig. 1. SEM images of the synthesized MSH powders.

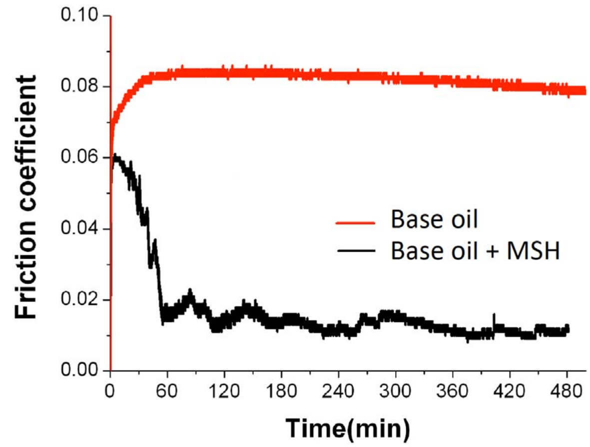

Fig. 2. Evolution of the coefficient of friction (COF) during friction tests for samples lubricated with pure base oil (red line) and the base oil with synthetic magnesium silicon hydroxide (MSH) additives (black line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

nanomaterials. More importantly, the simple, self-generating and highly adaptive tribolayer is formed directly from the lubricating oil molecules during normal operation of mechanical systems.

2. Experimental and materials

In this work we use synthetically-prepared MSH nanoparticles to achieve compositional uniformity and to add special functionality with the addition of catalytically active dopants (or elements that regulate the catalytic decomposition of oil molecules). The microstructure of the synthetic MSH nanoparticles is characterized by scanning electron microscopy (SEM) in Fig. 1.

For the preparation of the MSH nano-particles, we used a microwave-assisted hydrothermal synthesis process. 10% wt. Ni was doped to the MSH-oil as catalyst. During synthesis, finely ground forsterite and sodium metasilicate particles were mixed in a mechanical mixer and then subjected to a microwave-assisted hydrothermal process at 220 °C for 6 h to form MSH nano-powders. The resulting powders were washed in water for three times to remove sodium and dried in air. Microstructures of MSH were studied using SEM.

The powders were ultrasonically dispersed in polyalphaolefin base oil (PAO) with a viscosity of 32.4 cSt at 40 °C. The resulting oil-MSH suspension/colloid was then used for friction tests. The weight percentage of the powder in the oil-powder suspension was 0.3%. This concentration was optimized in previous studies. At this concentration, the viscosity of the oil was not affected at any measurable level. Friction tests were conducted on a Falex H-60 standard block-on-ring tribometer. The block and ring samples of 52100 steel with 62 HRC hardness were used. The ring rotation speed was 300 rpm and the mechanical load was 300 N, corresponding to a maximum pressure of 0.32 GPa and a speed of 0.549 m/s. Tests were run at room temperature with ~35% RH humidity. A SRV tribometer was used to examine the welding point of the lubricant with MSH. The upper specimen of 52100 steel ball (diameter 12.7 mm) reciprocated on the flat surface of 52100 steel with a frequency of 50 Hz. The stroke length was 5 mm. The load increased from 60 N with a step of 30 N every 2 min. The test stopped automatically as seizure occurred. The same lubricants as above block-on-ring tests were utilized.

TEM specimens were prepared using focused-ion beam approaches. TEM characterization was carried out using the Argonne Chromatic Aberration-corrected TEM (FEI Titan 80-300 ST) with a CEOS spherical and chromatic aberration corrector on the imaging side of the column operated at 80 kV to reduce beam damage to the film.

Chemical analysis of the tribofilm formed during sliding was performed with an Invia confocal Raman microscope using ultraviolet (UV) laser light (λ=325 nm). The UV light was selected in consideration of high sensitivity to carbon species and low fluorescence effect from oil contamination.

3. Results and discussion

3.1. Friction and wear

Fig. 2 shows the coefficient of friction (COF) from a steel test pair subjected to friction testing in pure base oil and base oil with the MSH additive (termed as MSH-oil in the following text). The COF of the sample tested in pure base oil is ~0.08 at steady state and remains steady until the end of the test. In contrast, the COF of the sample tested in MSH-oil decreases dramatically from an initial level of ~0.06 to ~0.01 at steady state. The dramatic decrease of friction during the initial run-in period is most likely due to the formation of a carbon-rich tribolayer on the rubbing surfaces. We believe a tribolayer forms first locally at asperity tips and then gradually expands in size and eventually covers the entire contact surface. After the tribolayer becomes continuous (after about 60 min), the COF begins to stabilize but still fluctuates occasionally between 0.02 and 0.01. Such fluctuations in COF with time are likely due to a self-generation and -organization mechanism of a low-shear tribolayer. The presence of a carbon-rich protective tribolayer on the samples tested with MSH additive was confirmed by electron microscopy, and Raman spectroscopy.

Fig. 3 shows plan-view optical microscopy images and 3D depth profiles of the wear grooves formed on the block side of the samples. The sample that was lubricated with MSH-oil had much narrower and smoother wear surface as compared to the sample that was tested in base oil. In addition, the wear groove for the MSH-oil lubricated sample was half depth of that for the sample tested in pure base oil, as shown in the 3D depth profiles. A grayish tribofilm on the rubbing surfaces of both block and ring samples was apparent. These results show that the addition of synthetic MSH leads to remarkably superior antiwear performance.

We used the thermoelastohydrodynamic lubrication (TEHL) model given in [17] to estimate the oil film between the block and ring under the same conditions as the above block/ring test, and the film thickness over contact area is between 0.14 μm and 0.08 μm shown in Fig. 4. The X axis and Y axis correspond to ring axial direction and ring rotating direction respectively in Fig. 4. The roughness of the wear track in the presence of MSH is about 0.1 μm. So the ratio of film thickness and roughness is between 1.4 and 0.8 which indicates the mixed lubrication occurs. Hence, we should not attribute the low friction to the pure hydrodynamic lubrication. From another aspect, the fluctuation of COF