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Oxidation Effects on the Friction of Lubricants and Self-Lubricating Materials in the Enduring Stockpile

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Abstract

Predictive models of solid lubricant performance are needed to determine the dynamic behavior of electromechanical devices after long periods of storage. X-ray photoelectron spectroscopy has been used to determine the kinetics of oxidation and sulfate formation for solid lubricants and self-lubricating materials containing MoS_2, exposed to a variety of oxidation conditions. The frictional performance of the lubricant has then been determined as a function of its surface chemistry and the ambient environment in which sliding takes place. Results indicate that surface sulfate formation governs the initial or start-up friction coefficient of MoS_2-containing films, while the composition of the ambient gas determines the steady-state friction coefficient. The dependence of the steady-state friction coefficient on the environment in which sliding takes place has been examined, and the results show that dynamic oxidation of surfaces having exposed metal has a major impact on friction. Surface oxidation is also shown to influence the frictional behavior of a self-lubricating composite material containing MoS_2.

Introduction

Reliable operation of electromechanical devices critical to nuclear weapon system performance requires consistent dynamic behavior of a mechanical timer. These electromechanical devices frequently employ films of solid lubricants to insure consistent lubrication over a wide range of temperatures, without migration during long periods of storage. The most ubiquitous solid lubricant in weapon electromechanical devices is a composite of MoS_2 and graphite powder, or "pigment," in an epoxy resin matrix. This lubricant is applied by manual or automatic spraying, cured, and then burnished to expose the lubricating pigment. Two different burnishing processes have been used historically. A process referred to in this work as "medium burnish" removes most of the lubricant with a wire brush, leaving about half of the metallic substrate exposed. The other process, referred to in this work as "light burnish," makes use of a solder flux brush to remove only the loosely-bound particles from the surface, and expose the solid lubricant pigment. This process leaves no substrate exposed. These materials and processes are used in the MC2969 Intent Stronglink, where the timing of the escapement subassembly is critically dependent upon the behavior of lubricated parts. Medium burnishing was used during early production of the MC2969, and light burnishing has been used only in the past five years.

A composite material containing 15 wt.% MoS_2 powder in a polyimide matrix is also used in the MC2969 Intent Stronglink. Known as Vespel SP3 (DuPont), a cam follower is made of this material, and makes contact with a stainless steel drive cam. During sliding, the Vespel material forms a surface transfer film of MoS_2 which controls friction at this interface. Recent dynamic simulations of the escapement subassembly have shown that changes in friction coefficient at the cam/follower interface have the largest impact on device operating time, followed by friction at journal bearing and gear surfaces where the resin-bonded film is present [1].

The purpose of this work is to examine the effects of the environment on the performance of lubricants used in weapon electromechanical devices, and develop the capability to predict changes in lubricant behavior as a function of age and environments that may be present. MoS_2 has been used for decades as a lubricant in aerospace applications, and is known to exhibit low friction coefficient (less than 0.1) in vacuum or inert gas environments. The presence of oxygen or water vapor in the atmosphere increases the friction coefficient of interfaces containing MoS_2. Although many weapon electromechanical devices are back-filled with some inert gas mixture and sealed, the specified leak rate is finite, and some reactive gases can enter the sealed volume over time. Oxygen and water vapor may interact with lubricants used in electromechanical devices to change their behavior. A lubricant aging model to describe this behavior can be included in a dynamic model of the device to determine the impact of changes in lubricant performance on device reliability.

Experimental

Lubricant aging results reported here come primarily from accelerated oxidation of sample coupons. These results are being correlated with data acquired on aged hardware returned from the stockpile. For the resin-bonded lubricant, coupons 1 mm thick and 25 mm in diameter of 15-5PH stainless steel and Cu-2% Be alloys (the predominant substrates for this material in the application) were prepared and cleaned per production specifications. After deposition and curing of the lubricant the surfaces were burnished for subsequent analysis. For the self-lubricating composite, coupons about 1 mm thick were cut from a rod 13 mm in diameter and subjected to aging. Accelerated aging for both types of materials was carried out in an oven where the water vapor concentration could be controlled. Surface composition measurements were made using x-ray photoelectron spectroscopy (XPS) with a PHI 3057 system. Spectra were acquired using Al irradiation at 15 keV and 600 W target power. Friction coefficient measurements were performed using a custom pin-on-disk friction measurement apparatus that operates in a controlled environment at atmospheric pressure. In these experiments, a polished ball (arithmetic average roughness of 20 nm) of 440C steel 1.6 mm in diameter was brought into contact with the lubricated flat under loads of 32 gf, to produce a peak contact stresses of ~ 1 GPa. Sliding speeds were in the range of 10-20 mm/s, and sliding was continued for 1000 cycles, after which a steady-state friction coefficient was usually exhibited.

Results and Discussion

Since the gaseous environment inside electromechanical devices may contain various amounts of water vapor and oxygen after long periods of storage, the effect of water vapor concentration on friction coefficient has been examined. The initial and final (steady-state) friction coefficient as a function of the water vapor concentration in nitrogen for non-aged, medium burnished lubricant on stainless steel are shown in Figure 1. The data is presented as box plots, where the central symbol is the average value, the box bounds represent the 25th and 75th percentiles, and the symbols outside the box represent the maximum and minimum observed values. This substrate/burnish combination exhibited the greatest variation between initial and final friction coefficient at high water vapor concentrations. Lightly burnished lubricant on stainless steel and both burnishes on Cu-2% Be showed no more than a factor of two change in friction from the initial to steady-state values, even at high humidity. Previous work has shown that the presence of metal oxides promotes more rapid oxidation of the MoS_2 under static conditions [2]. Similarly, more rapid oxidation of the MoS_2 would be expected on a medium-burnished surface compared to the lightly-burnished surface in the dynamic situation, where oxide removal by wear is occurring simultaneously with oxidation. Oxidation results in disruption of the low shear strength lamellar structure of the film, and hence higher friction coefficients. The data suggest that oxides of iron and chromium on stainless steel are much more effective than copper and

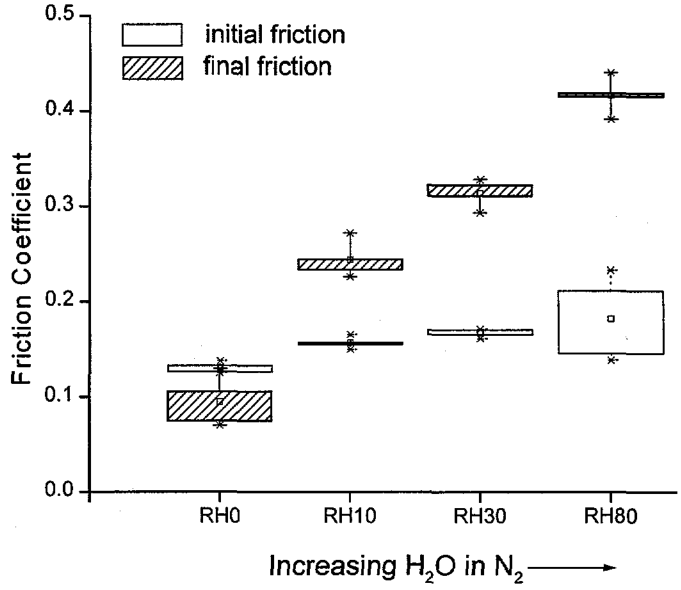

Figure 1. Initial and final (after 1000 cycles) friction coefficient for medium-burnished film of resin-bonded lubricant on 15-5 PH stainless steel, as a function of water vapor content in nitrogen. See text for discussion.

beryllium oxides in promoting dynamic oxidation of MoS_2 during sliding. Clearly the environment present *at the time of use* will have significant impact on the friction coefficient at contact locations. The relative impact of the different metal oxides on the oxidation kinetics of MoS_2 is the subject of continuing research.

Coupons of Vespel self-lubricating composite were exposed to 150°C air for up to one week to determine if the tribological behavior of this material could be influenced by oxidation. Accelerated aging of the Vespel has shown that the friction coefficient exhibited during sliding contact of this surface with a steel ball is influenced by surface oxidation. Figure 2 shows that the friction coefficient exhibited by non-oxidized Vespel in nitrogen is 0.3. After just one hour of exposure to the oxidizing environment, the initial and steady-state friction coefficients increase to nearly 0.5. In this case, friction coefficient was measured in a nitrogen environment after oxidation of the material, so these changes are due to changes in the surface composition of the Vespel that persist during wear of the material in an inert environment. The lubricating mechanism of Vespel involves shearing of the entrained MoS_2 particles near the surface to form a layer on top of the polyimide matrix where sliding takes place. This "transfer film" is easily formed in nitrogen, where the MoS_2 maintains its lamellar structure having low-shear planes terminated in sulfur atoms. After oxidation of the MoS_2 particles near the surface, the low shear hexagonal structure of MoS_2 is lost to formation of MoO_3. We postulate that this oxidation inhibits formation of a transfer film to cover the polyimide matrix, and so the measured friction coefficient is dominated by interactions between the polyimide and the steel ball. This conclusion is supported by the fact that friction coefficients measured between neat polyimide and steel are in the range of those observed for the MoS_2-filled and oxidized material, and the friction coefficient exhibited by the neat polyimide does not vary significantly with oxidation under the same conditions. Surface chemical analysis is under way to support this hypothesis, and to determine the kinetics of oxidation of the MoS_2 particles in the polyimide matrix so that a time-dependent degradation model for this material can be developed.

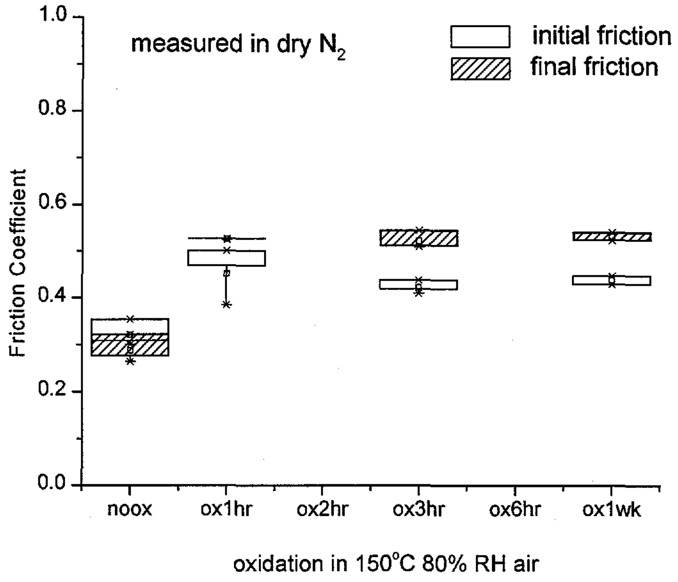

Figure 2. Initial and final (after 1000 cycles) friction coefficient for Vespel SP3 (polyimide + 15wt.% MoS_2) in contact with a 440C steel ball in nitrigen, as a function of static oxidation time in humid air.

Conclusions

Predictions for the performance of lubricated surfaces during extended service life applications require a thorough knowledge of material degradation mechanisms and kinetics. In an effort to develop age-dependent dynamic models for device behavior, a detailed examination of lubricants used in the MC2969 Intent Stronglink is in process. This component was chosen due to the sensitivity of the timing mechanism to lubricant performance, the presence of these mechanisms in over half of the enduring stockpile, availability of aged hardware from dismantlement activities and the fact that component failure translates directly into failure of the entire weapon system. Degradation of the solid lubricants and self-lubricating composites examined to date is attributable to oxidation of MoS_2 within the materials, in the presence of oxygen or water vapor in the environment. For burnished films containing MoS_2 on metallic substrates, static surface oxidation affects the initial friction coefficient, and the composition of the gas in which the device is operated has the greatest impact on the steady-state friction coefficient through dynamic oxidation of the lubricant. For Vespel, static oxidation of near-surface MoS_2 particles inhibits transfer film formation, so that the interaction between polyimide and the counterface dominates the friction response. Work continues to quantify reaction kinetics in order to provide materials aging predications for service life extension.

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