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Aging Model for Solid Lubricants Used in Weapon Stronglinks: Oxidation Chemistry and Hardware Review

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Abstract

In support of efforts to model the performance of the MC2969 stronglink for stockpile life extension, the kinetics of oxidation of the MoS_2-based solid lubricant coating have been determined. The lubricant oxidation is primarily influenced by the extent of burnishing of the coating after application and curing. The activation energy for lubricant oxidation is low and agrees well with reported values for MoS_2 coatings and particles. The type of substrate material and the amount of H_2O vapor present have little influence on the oxidation kinetics, but do affect the chemical species found on the surface, including sulfate species which enhance substrate corrosion. The analysis of field-returned hardware shows oxidation levels within the range of those obtained throughout the oxidation study.

Introduction

Science-based stockpile stewardship and lifetime extension predictions require physical-based models of materials aging issues and their influence on component and weapon system performance. One of the key weapon systems safety elements is the MC2969 Intent Stronglink. The escapement assembly contained in the MC2969 contains a series of lubricated gear assemblies, which must operate within a well-defined time period in order for proper signal discrimination to occur. Changes in lubricant performance during long term storage can adversely affect the escapement timing, and consequently, operation of the entire MC2969 functionality. This work is part of an integrated effort to develop a model for predicting the performance of the MC2969 escapement assembly after long-term exposure to conditions in the stockpile, and in turn, to assess the impact of stockpile life extension on the MC2969 reliability. In support of this modeling effort, we have completed a series of experiments designed to understand the oxidation kinetics and mechanisms of the solid film lubricant used on the MC2969 escapement gear assemblies.

The MC2969 escapement assembly utilizes a resin-bonded solid lubricant that contains particles of graphite and MoS_2. Films of pure MoS_2 are known to oxidize after long term static exposure to O_2 or H_2O vapor, causing an increase in the friction coefficient and wear rate. In addition, the dynamic steady-state friction coefficient of pure MoS_2 films is increased by testing in the presence of O_2 and H_2O vapor. While oxidation of crystalline MoS_2 and sputtered MoS_2 thin films has been extensively studied in a range of environments,[1-4] the oxidation kinetics of MoS_2 in a resin-bonded composite, and the effect of oxidation of the composite film on tribological performance, are not known. Water vapor, type of substrate, amount of substrate material exposed on the surface, and the presence of other adsorbates can all affect the oxidation kinetics and performance of the solid lubricant coating. The relative importance of these factors must be determined in order to implement physical-based performance models. This work reports our efforts to understand the effects of each of these parameters on the oxidation kinetics and mechanisms of MoS_2 within the resin-bonded lubricant matrix.

Experimental Procedure

Sample disks were prepared from 15-5PH stainless steel and Cu-2%Be alloy, which were lapped, wet blasted with an alumina slurry and cleaned. Once prepared, the coupons were coated with a heat-cured resin-bonded solid lubricant containing MoS_2 and graphite particles, manufactured at Allied Signal/FM&T. This material is identical to that used during the past 20 years in stronglink production, but was formulated and produced in-house to improve quality control and to replace the commercial formulation which is no longer available. The lubricant was sprayed onto the coupons to a thickness of 25 μm, allowed to air dry, and oven cured at 200°C. After curing of the lubricant coating, the sample coupons were burnished in order to remove loosely adhered particles and the overlying resin-bonding layer from the surface. Two different burnishing procedures were used to duplicate old, as well as current, stronglink lubricant application specifications. A "light burnish" was produced by gently burnishing the samples by hand with an acid solder flux brush. A more aggressive "medium burnish" was produced using a stainless steel wire brush in a rotary tool, which results in significant exposure of the underlying substrate material. In both cases, the surface can be processed to a well controlled end point, where the surface exhibits a uniform color and reflectivity. After burnishing, the sample coupons were oxidized at temperatures of 60°C to 200°C.

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After burnishing and oxidation exposures, the sample coatings were analyzed by x-ray photoelectron spectroscopy (XPS) to determine the elemental composition of the near surface layer and the oxidation state of the chemical species present. Survey scans were used to identify the atomic species present, and detailed high resolution scans for each element were used to determine chemical state information and quantitative surface composition information. Standard sensitivity factors were used[5] to calculate elemental compositions. Where detailed chemical state information was desired, peak fitting was used to identify ratios of chemical species present. In particular, details of the Mo 3p, O 1s and S 2p peaks were used to assess the oxidation of the MoS_2 particles within the lubricant coating.

Field-returned hardware was also analyzed from MC2969 stronglink escapement assemblies to ascertain a snapshot of the surface chemistry and oxidation levels of the lubricant films present in the field. These units were opened in a clean bench after the enclosed gas had been carefully sampled. The parts were immediately packaged with desiccant to minimize changes in the lubricant coating due to reaction with atmospheric contaminants and water vapor. XPS analysis was completed for each of the 2 CuBe gear assemblies, the CuBe star wheel, and the stainless steel drive cam and timing follower reset assemblies. To date, the individual piece parts from a total of 12 stronglink escapement assemblies of varying ages and environmental conditions have been examined, including hardware 9 to 20 years of age.

Results and Discussion

The solid lubricant coating contains MoS_2 and graphite particles 10 to 20 μm in size, distributed throughout the resin-bonded matrix. Since the size of the particles is a large fraction of the coating thickness (25 μm), the appearance and morphology of the coating changes dramatically as a function of burnish. The unburnished coatings show particles typical of the distribution size range, but contain only C and O in the near surface region from the overlying resin-bonded matrix. After a light burnish, the loosely attached particles are removed, resulting in a much smoother surface. The near surface region of this bulk coating shows C, O and small amounts of Mo and S. After a medium burnish, many of the exposed lubricant particles have been smeared out, exposing a significant amount of the substrate material through voids. The near surface region of this coating shows reduced amounts of C, Mo and S, a slightly increased amount of O, and significant concentrations of the substrate material. It is believed that the medium burnished surface is very inhomogeneous, with areas of essentially bare substrate material and areas of lubricant coating with a thickness corresponding to the individual particle sizes present in the lubricant mixture.

The kinetics of oxidation of MoS_2 particles in the solid lubricant have been determined by oxidation in laboratory air as a function of temperature and burnish condition on stainless steel coupons. Sample coupons were oxidized in a bench oven using ambient laboratory air. The surface chemistry of the oxidized coatings was then measured to obtain the percentage of Mo present as the oxide, representing the amount transformed from the sulfide. Oxidation is initially rapid, slowing with time as the surface layers passivates. Plots of the percentage of Mo present as the oxide as a function of time for each temperature yield the rate of oxidation of the MoS_2 particles from the initial linear slope. From an Arrhenius plot of this data, shown in Figure 1, the activation energy for oxidation was determined to be 3.8 and 5.0 kcal/mole for the medium and lightly burnished coatings, respectively. Previously reported values of the activation energy for oxidation of pure MoS_2 include similar values of 5.5 kcal/mole[6] and 7.3 kcal/mole[7]. These activation energies are very low, signifying that MoS_2 oxidation has a very limited dependence on temperature and the resin-bonded matrix. However, the activation energy is lower, oxidation proceeds faster, and higher oxidation levels are obtained for the medium burnished surface relative to the lightly burnished surface. The calculated numbers for activation energy, pre-exponential factor and initial rates may be used to estimate oxidation times as a function of burnish condition.

In order to assess the relative importance of substrate material and the presence of H_2O vapor on oxidation kinetics, a matrix screening study was conducted. Medium burnished samples were used to predict the "worst case" response, since medium burnished samples oxidize faster and substrate materials are exposed to participate in any reactions that occur. For this study, sample coupons were oxidized in a controlled atmosphere oven, which utilized dried air that had been re-humidified to produce the desired mix of oxygen and water vapor. The rate of oxidation is not strongly affected by the amount of water vapor present, the type of substrate material or temperature, but these parameters do impact the chemical species formed during oxidation. Reaction pathways between the lubricant, substrate and gases are shown in Figure 2. Reaction of the lubricant with oxygen produces surface sulfates and may result in a reduction in total sulfur by volatilization of reaction products. When water vapor is present, sulfates react with water to form corrosive products that can attack exposed substrate material and cause formation of metal oxides at the surface. This reaction is facilitated by the tendency of the substrate metal atoms to diffuse to the surface under the presence of reactive atmospheres. These reactions have the potential to dramatically change the sliding friction behavior of the surfaces.

The review of lubricated stronglink assemblies has shown that most of the parts have between 30% and 60% of the MoS_2 in the near surface region oxidized. These values are well within the range examined by oxidizing the sample coupons, showing that the model oxidation studies are producing reasonable oxidation levels. Typically, the stainless steel parts of the escapement assemblies show higher oxidation levels that those present on the CuBe parts, possibly because of the presence of an overcoat of Vydax fluorocarbon lubricant that is applied to the CuBe parts. Although the S to Mo ratio is essentially the same for CuBe and stainless steel parts examined, the stainless steel parts consistently show more Mo and S than the CuBe parts, another possible consequence of the Vydax overlayer. Some of the older units show noticeable buildups of sulfates on the surface and some oxidation of the visible substrate material.

Conclusions

To facilitate stockpile life extension predictions, an integrated study has been designed to model the performance of the MC2969 stronglink escapement assembly from materials aging issues to device performance levels. As a part of this effort, the kinetics of oxidation of the solid lubricant coating used on the MC2969 escapement assemblies have been determined. The oxidation of the MoS_2 contained within the lubricant coating is primarily influenced by the extent of burnishing of the coating after application and curing. The activation energy for lubricant oxidation is low, 3.8 and 5.0 kcal/mole for medium and lightly burnished surfaces, respectively. These numbers agree well with reported values for oxidation of MoS_2 coatings and particles. The type of substrate material and the amount of H_2O vapor present have little influence on the oxidation kinetics, but do affect the chemical species found on the surface as a result of oxidation, including sulfate species which enhance substrate corrosion. The analysis of field-returned hardware shows oxidation levels within the range of those obtained throughout the oxidation study, validating the methods and results obtained from this work. These results may be used to estimate the extent of lubricant oxidation as a function of burnish, time and environment - the initial step in obtaining an integrated performance model for the MC2969 stronglink.

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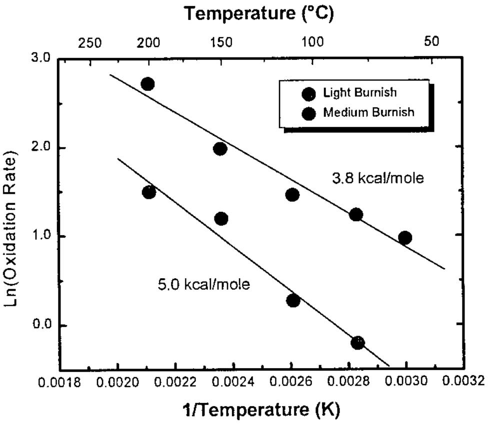

Figure 1: Arrhenius plot for the initial oxidation rate of MoS_2 particles within the coating as a function of type of burnish.

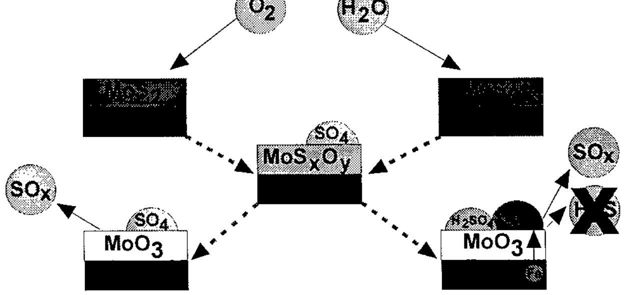

Figure 2: Schematic of reaction mechanisms and products for the lubricant coating in the present of O_2 and H_2O vapor.

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