SYNERGISTIC EFFECTS OF LIQUID AND BORIC ACID SOLID LUBRICANT FILMS ON FRICTION AND WEAR OF SLIDING STEEL SURFACES

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ABSTRACT

This study explores the synergistic effects of liquid and solid boric acid lubricated steel surfaces on friction and wear performance of sliding steel surfaces. Specifically, test conditions were adjusted to provide a boundary lubricated sliding contact regime, so that the synergistic effects of solid and liquid boundary films could be discerned. High purity boric acid films were formed on boron carbide surfaces by a simple annealing procedure at 800 °C for 15 min. Subsequently, the coated samples were cooled to room temperature and tested in a pin-on-disk machine under dry and lubricated sliding conditions. During annealing, boron carbide reacts with oxygen in air and forms a glassy boron oxide (B2O3) layer on the exposed surface. This B2O3 layer reacts spontaneously with moisture in the surrounding air, thus forming a thin boric acid (H3BO3) film. The friction coefficients of 52100 steel pins against the substrate material (B4C) are 0.4-0.8 under dry sliding conditions. The friction coefficients of 52100 steel pins against boric acid film are 0.04-0.06 under dry-sliding conditions, but with the introduction of a pure paraffinic oil to the sliding interface, the friction coefficients drop 0.01. Electron microscopy and Raman spectroscopy were used to elucidate the formation and self-lubricating mechanisms of the boundary films present on sliding surfaces.

INTRODUCTION

Previous studies have confirmed that boric acid (H3BO3) is an effective solid lubricant with friction coefficients as low as 0.02 under dry-sliding conditions in open air. This solid can be used to lubricate sliding surfaces in a variety of ways. The simplest, but least practical way is to spread over or sprinkle fine powders of H3BO3 on a sliding surface that needs lubrication. Alternatively, thin solid films of H3BO3 may be formed on surfaces to be lubricated or fine powders of H3BO3 can be mixed with metal, ceramic, or polymer, matrices to achieve self-lubricating composites. Studies over the years have demonstrated that regardless of the form used, H3BO3-based solid lubricant films can afford low friction coefficients and high-wear resistance to sliding contact interfaces of metallic, ceramic, and polymeric tribomaterials.

The self-lubricating action of H3BO3 is due to its unique layered crystalline structure. Specifically, it provides lubrication by an interlayer shear mechanism. In its triclinic crystal structure, the boron, oxygen, and hydrogen atoms lying on the same plane are closely packed and strongly bonded to each other to form a rigid layer. The atomic planes are relatively far apart (0.318 nm) and the forces that bond them, e.g. van der Walls, are weak. Strong interatomic bonding and packaging in each plane give H3BO3 the very high in-plane strength that is essential for long wear life or reduced-wear during sliding, while wide interlayer spacing and weak bonding insure easy shear. When present on a sliding surface, crystalline layers of H3BO3 align themselves parallel to the direction of relative motion and slide over one another with relative easy to provide lubrication.

More recent studies have revealed that H3BO3 films can spontaneously form a tribologic surface mainly because the heat of reaction between these surfaces, H3BO3 and moisture in air is negative. Formation of such self-lubricating and self-replenishing films was also demonstrated on certain borides (such as VB2), B4C, and borided steel surfaces.

In this paper, a new lubrication method based on a self-replenishing H3BO3 film, and a pure paraffinic oil is introduced, and the synergistic effects of using such solid-liquid lubrication on friction and wear of sliding-steel surfaces are explored. The self-replenishing H3BO3 films were formed on B4C surfaces and the pure mineral oil was simply spread over the sliding surfaces. Raman spectroscopy was used to investigate the chemical structure of the lubricious surface films.

EXPERIMENTAL DETAILS

The initial flat substrates were made of H13 steel. They were cut into rectangular shapes with nominal dimensions of 50.8 x 37 x 6 mm. The surface finish of the test pieces was 0.1 um center-line-average (CLA). Coating surfaces of B4C were deposited on H13 flats by magnetron sputtering. The B4C samples had a surface finish of 0.1-0.2 um CLA. Pure compositions of self-replenishing H3BO3 films were formed by annealing the B4C surfaces at 800°C for 15 min and them removing them from the furnace and cooling to room temperature in open air.

Friction and wear testing of the coated and “as-received” steel samples was carried out in a pin-on-disk tribometer under 10 N load at room temperature (23°C). The relative humidity of the test chamber was 50-60%. Rotational velocity was 5-10 rev. min^{-1}, which translated into a sliding velocity of 0.05-0.08 m.s. $^{-1}$. The sliding distance was 500m. Such a low-sliding velocity and a high-contact load were specifically selected to achieve and maintain a boundary-lubrication regime so that the high-contact load were specifically selected to achieve and maintain a boundary-lubrication regime so that the effectiveness of the solid lubricant H3BO3 films are observed. The counterface materials were made of 52100 steel pins (9.5 mm in diameter). One end of each pin was rounded to a radius of curvature of 127mm and used as the contact surface. They were polished to a surface finish of 0.01 um CLA roughness. The pins were firmly secured to a stationary holder for the pin-on-disk configuration. Flat subsrates were attached to a horizontal chuck driven by a variable-speed electric motor. Frictional force was monitored by a linear-voltage displacement transducer attached to the ball holder and was recorded continuously. Before each sliding test and annealing heat treatment, the steel flats were cleaned ultrasonically in acetone and methanol for 300 s each and then oven dried at 110°C for 10 min. Laser Raman spectroscopy was used to characterize the structure and chemical nature of the sliding surfaces. The Raman spectroscope was an HeNe laser at 632.8 nm with an output power of 25 m W focused to a spot size of 2-3 um. Duplicate tests were run with “as-received” and annealed B4C coatings to check the reproducibility of test results.

RESULTS AND DISCUSSION

The B4C surfaces tested in this study had a dense columnar structure and were about 2 um thick. Raman spectroscopy of the “as-received” as well as annealed B4C surfaces revealed that in the “as-received” condition, there were no discernible Raman bands within the range examined as shown in Fig. 1; however, after annealing the B4C surface exhibited three strong Raman bands centered at around 220, 500, and 800 cm^{-1} as shown in Fig. 1. These all corresponded to the Raman bands of a reagent-grade H3BO3 standard that is also included in Fig. 1. for comparison. In short, these findings confirmed that the near region of the B4C surface transformed to H3BO3 after the annealing heat treatment as elaborated in the Experimental Details.

The conversion of near-surface region of B4C to H3BO3 has been explained in earlier papers. Briefly, boron atoms at or near the surface of B4C become thermally active and ready to react with oxygen in the surrounding air during annealing at 800°C. The reaction product is boron oxide (B2O3) which when exposed to moist air, reacts spontaneously with water molecules in surrounding air to form a thin H3BO3 film on its surface. This is mainly because the standard heat of reaction for B2O3 and moisture (h2O0 is negative at room temperature.

DRY- SLIDING TESTS

Figure 2 presents the friction coefficients of 52100 pins during sliding against B4C-coated steel flats before and after annealing at 800°C for 15 min. These tests were run under dry-sliding conditions. The friction coefficient against “as-received” B4C surface us initially 0.4, but increases substantially with sliding distance especially beyond 100 m and reaches a value of =0.8 toward the end of the test. The initially low friction coefficient of B4C surface may have been due to the presence of an absorbed or contaminant layer on its sliding surface and on pin. As the contaminant layers wear out, the sliding increasingly occurs between steel pin and B4C material and this causes increasingly higher friction.

Figs. 3a and 3b shows the conditions of the wear scar and track formed on sliding steel pin and B4c coating, respectively. It appears that the sliding surface of the steel pin suffered a significant amount of wear (see fig. 3a) during dry-sliding. Using a mathematical formula, the diameter of the wear scar shown in Fig. 3a was used to assess first the wear volume and then the wear rate. The wear rate of the 52100 steel pin against the “as-received” B4C surface was found to be 2.2x10^-5mm^3/N.m. The amount of wear on B4C surface was hard to measure, but some debris particles were present and appeared to have been smeared on the sliding wear track of the B4C surface as shown in Fig. 3b. This suggests that the sliding was perhaps partially taking place between these trapped or smeared debris particles and the surface of the steel pin and hence the increasingly higher friction coefficient seen in Fig. 1 may have been partially due to the presence of such debris layer at the sliding interface.

The sliding friction coefficient of steel pin against the spontaneously deposited H3Bo3 coated B4C surface is initially 0.08, but decreases to 0.05 further sliding and remains constant for the duration of test (See Fig. 2). This means a 16-fold reduction in the friction coefficient of the “as-received” B4C surface. The mechanistic explanation for such a drastic reduction in friction is that after annealing, the sliding surface of B4C is covered with a layer of H3BO3 having a layered crystal structure as illustrated in Fig. 4. The atomic layers are made of strongly bonded boron, oxygen, and hydrogen atoms; they are 0.318 nm apart and held together by weak van der Waals forces. When present at a sliding interface, these layers shear easily to provide low friction.

Fig. 5 shows the condition of steel pin after sliding against H3BO3 coated B4C surface. There is no evidence of the formation of a flat and circular wear scar on this pin at the magnification shown in Fig. 5a, but it appears that a transfer layer is present in and around the leading as well a trailing edges of the wear scar. 3D surface profile taken after the removal of this layer (by means of ultrasonic cleaning in an acetone bath) indicates that the pin surface did not rally suffer much wear and that the original spherical shape of the pin surface was still intact. Therefore, a reliable quantitative assessment of the wear volume and wear rate was not possible on this steel pin. Microscopic inspection of the wear tracks formed on the B4C surfaces revealed that both the “as-received” and H3BO3 coated B4C surface did not suffer much wear, but some debris particles (mostly from the pin side) were present in and around the wear tracks of the “as-received” B4C surface. Overall, the results of dry-sliding test confirmed that the friction and wear performance of steel pins against B4C surfaces is rather poor, but it can be improved substantially by the introduction of an H4BO3 film layer.

LUBRICATED TESTS

Fig. 6 shows the friction coefficients of 52100 steel pins during sliding against “as-received” and annealed B4C surface under lubricated test conditions. The friction coefficient of “as-received” B4C surface is 0.12 at the start and remains essentially constant for the duration of sliding test. However the friction coefficient of an H3BO3 coated B4C surface is 0.06 at the start, but decreases steadily with further sliding and eventually reaches a steady state value of 0.008. This means more than an order of magnitude reduction in friction coefficient. Again, the only difference between the “as-received” and H3BO3 coated B4C surfaces is the presence of a lubricious H3BO3 film.

The size and morphology of wear scar formed on the 52100 steel pin side after lubricated sliding against the “as-received” B4C is shown in Fig. 7a. Converting this wear scar into wear rate, one obtains a value of 4.7x10^-7 mm^3/N.m. Note that this wear rate is by a factor of 4.6 smaller than that f the pin slide against the B4C surface under dry-sliding condition. The wear scar formed on steel pin after lubricated sliding test against the H3BO3 coated B4C is hard to discern (see Fig. 7b) suggesting that the H3BO3 film formed on the surface does not cause much wear on the sliding pin counterface. Since there was no measurable wear scar on this pin, it was difficult to assess its wear rate.

The results presented above indicate that combined use of liquid lubricant with a self-forming and replenishing solid-lubricant film (i.e., H3BO3) provides very low-friction coefficients and wear rates to sliding-metal surfaces. Specifically, it has a beneficial synergistic effect on the friction and wears performance of sliding surfaces. The logical explanation for this is that because of its low shear character, the H3BO3 layer on the sliding surface shears easily during sliding contact and eventually reaches a very smooth and highly conformal state. As can be seen from Fig. 6, the initial friction coefficient of the steel pin against the H3BO3 coated B4G surface is 0.05, but decreased progressively with the further sliding to values as low as 0.01. This suggests that the sliding contact surface became increasingly smoother during successive sliding passes. As elaborated in basic lubrication textbooks, a smooth surface finish in a lubricated contact always results in an increased ^ ratio (the ratio of the minimum elastohydrodynamic film thickness [h] to the composite surface roughness [s] of the contacting bodies, ^=h/s). When the ^ ratio increases (due to reduced surface roughness), the effectiveness of the lubricant oil increases significantly. This is particularly true for cases where ^ is equal to or greater than unity, which means that the lubricant film thickness is greater than the composite surface roughness of the contacting bodies; hence asperity/asperity interactions through the lubricant film are minimized. Under such sliding situations, the friction coefficients are largely determined by the shear rheology and/or viscosity of the lubricant oil. Even if there was some direct asperity/asperity contact across the sliding interface, H3BO3 mainly because of its low shear strength could shear easily and provide low friction by acting as an effective boundary film lubricant.

Overall, the results of dry and lubricated test presented above indicate that H3BO3 alone is rather effective in reducing friction between sliding surfaces but when combined with a liquid lubricant, it can impart further reductions in friction. This finding suggests that solid dispersion of H3BO3 in oils and greases may have a beneficial synergistic effect on friction and wear of sliding surfaces. Obviously, more experimental and analytical works should be done to elucidate this and other possibilities in the near future.

CONCLUSION

1. Thin H3BO3 films formed on substrate surfaces provide very low-friction coefficients (0.05) and wear rates to sliding-steel surfaces.

2. Mechanistically, the low-friction character of the H3BO3 film formed on substitute material is due to its layered crystal structure. Specifically, under the influence of shear

forces, the atomic layers of H_3BO_3 align themselves parallel to the direction of sliding motion and then slide one over another to provide the levels of friction coefficients reported in Fig.2.

3. The combined use of a liquid lubricant with H_3BO_3 films on a sliding surface can significantly reduce friction and wear.

4. It is proposed that the beneficial synergistic effect observed under lubricated test conditions is due to the formation of an increasingly smooth H_3BO_3 surface finish on the substrate material which progressively results in an increased ^ ratio that in turn can lead to a more efficient lubrication regime in which asperity/asperity interactions through the lubricant film are minimized.