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TRIBOLOGICKÉ VLASTNOSTI NANÁŠANÝCH VRSTIEV TUHÝCH MAZÍV OVEROVANÉ V ATMOSFÉRE A VO VÁKUU

TRIBOLOGICAL BEHAVIOR OF BONDED SOLID LUBRICANT FILM IN AIR AND IN VACUUM

Trecie testy inorganicky viazaných kompozitných vrstiev tuhých mazív (WS_2, grafit, BN) boli uskutočnené v laboratórnych podmienkach v atmosfére a vo vákuu v rozsahu 10^{-4} Pa.

Stopy opotrebenia a prenos vrstiev boli vyšetrované rastrovacím elektronovým mikroskopom a Augerovou elektronovou spektroskopiou.

Z experimentálnych výsledkov vyplýva, že pre testy uskutočnené v atmosfére v laboratórnych podmienkach si dominantné postavenie zachovávajú vrstvy grafitové. Vo vákuu má rozhodujúci vplyv WS_2 vrstva. Počas zmien z atmosféry na vákuum a opačne, kompozitné vrstvy preukázali lepšie trecie charakteristiky vo vákuu ako v atmosfére.

The friction tests of inorganic bonded composite solid lubricant films (WS_2, graphite, BN) were performed in laboratory air and in 10^{-4} Pa vacuum. The wear traces and transfer films were characterized by scanning electron microscopy (SEM), and Auger electron spectroscopy (AES). Experimental results suggest that when friction tests were conducted in air, graphite plays a governing role, while in vacuum WS_2 plays a governing role. In case of changing atmosphere from air to vacuum or from vacuum to air, the composite film showed better friction behaviors in vacuum than in air.

1. Introduction

Hexagonal boron nitride, graphite, molybdenum disulfide and tungsten disulfide belong to lamella solid lubricants. The crystal structures of these solid lubricants are such that while the atoms lying on the same layer are closely packed and strongly bonded to each other, the layers themselves are relatively far apart and the bond between them, e.g., van der Waals, are weak. When these lamella solid lubricants are present between sliding surfaces, these layers can align themselves parallel to the direction of relative motion and slide over one another with relative ease, thus providing low friction[1]. In addition, strong interatomic bonding and pack in each layer is thought to help reduce wear damage [2 - 4].

Many studies indicate that environment can strongly affect these solid lubricants. For example, graphite and boron nitride were found to lubricate better in humid environments than in dry environments; whereas MoS_2 and WS_2, were found to lubricate better in dry and in vacuum environment [5 - 6]. In recent years some experiments have been conducted to evaluate the synergistic effect of different kinds of lubricants. For example, the composite film of boron nitride and graphite could provide adequate lubrication from room temperature to 800 °C in air. While at low temperature graphite can provide lubrication, BN does so over 500 °C, graphite gets oxidized at high temperature [7].

It was also found that the addition of graphite to bonded MoS_2 film could enhance wear life of such films in air [8]. Moreover there are other composite lubricants comprising of MoS_2 and other synergistic agents, which show lower friction coefficient than those containing MoS_2 alone [9 - 11]. But for various solid lubricants the tribological mechanisms are not clear as detailed.

The major objective of this study is therefore to understand the friction mechanisms of solid lubricant composites in different environments. In this work, the solid lubricant WS_2 which is more stable and has better oxidation resistance than MoS_2 [12 - 13], BN and graphite (1:1:1), which are reported to have synergistic effects [7] were employed having ratios of WS_2: BN: graphite as 1:1:1.

Mica and sodium silicate are used as inorganic binder to avoid reaction between the binder and solid lubricants.

2. Experimental procedures

Friction tests were performed in a ball-on disk configuration. The ball 3 mm in diameter is made of high carbon chromium steel (SUJ-2) and disk 26 mm in diameter is made of stainless steel (SUS304). In order to increase the adherence of solid lubricant films, the surface of disk was abraded with No. 220 alumina sand blast. Then the solid lubricant film was formed with 50 % solid

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lubricant (WS_2, BN, graphite individual and composite with ratio of WS_2: BN: graphite as 1:1:1), 50 % inorganic bonded (mica: $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$, sodium silicate: $Na_2O \cdot 3.1SiO_2 \cdot xH_2O$), dried at 250 °C for 90 minutes in air. After the treatment the thickness of the film was about 15 μm.

The apparatus used in this investigation is shown schematically in Fig. 1. The evacuating system is consisted of an oil-sealed rotary pump and turbo pump. Three steel balls were buried in the tip of the slider and rotated co-axially on the disk. The disk was mounted on gimbals so that the balls could be rotated with the same load and set into the same orbit. The diameter of rotation was 20 mm, and the speed of rotation was controlled to 9 mm/sec. The load was 1.8 N (0.6 N each ball). The friction force was measured by strain gauge attached to the leaf spring. For wear life test in air as well as in vacuum, the apparatus was set up in such a way that as soon as friction abrupt increased the test was terminated. This condition signaled metal-to-metal (between the substrate of disk and the ball) contact due to solid lubricant film breakdown.

In case of friction test in vacuum, the chamber was subjected to vacuum to 10^{-4} Pa for six hours before the actual start of the experiment. For composite film the tests were conducted in alternate sequence (vacuum/air or air/vacuum) of 500 cycles for each environment with a maximum of 4 changes(4 hours). The relative humidity of the environment was approximately 60 - 75 % in air.

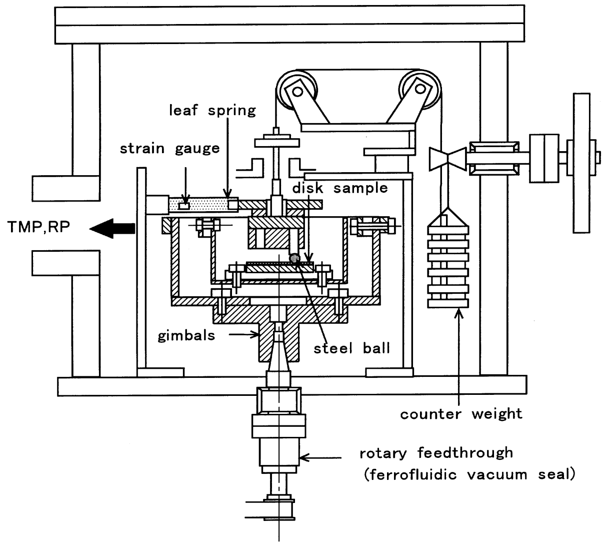

Fig. 1

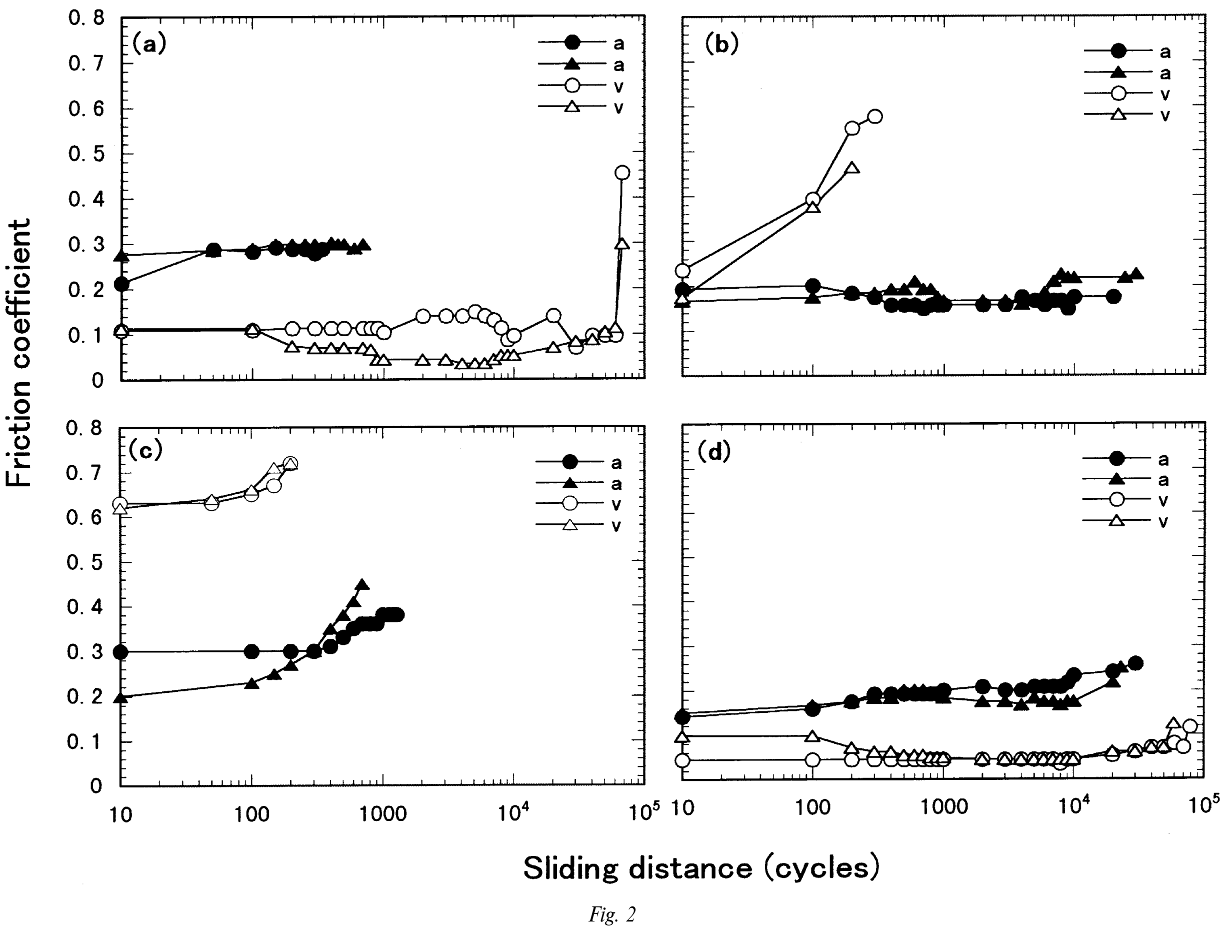

Fig. 2

3. Experimental results

Figure 2 shows the sliding distance versus friction coefficient in air and in vacuum for individual or composite films. In each case, at least two measurements were made. It can be seen that: (a) The friction coefficient for WS_2 film was about 0.1 in vacuum and about 0.3 in air. The endurance life is also affected by environment and though the film lasts for 68000 cycles in vacuum, it was less than 750 cycles in air. (b) Graphite film shows low friction coefficient about 0.2 in air with an endurance life of 25000-30000 cycles. In vacuum, however, the friction coefficient increased at quite an early stage from 0.2 to 0.6 and the endurance life was less than 250 cycles. (c) For BN film, the friction coefficient was 0.6 in vacuum and 0.2-0.3 in air, but in both environments the endurance life were less than 1000cycles. (d) For composite film, the friction coefficient was 0.06 in vacuum and 0.2 in air, the endurance life reached 59000-70000 cycles in vacuum and 23000-37000 cycles in air. Thus the composite films showed nearly the same friction behaviors as graphite in air, and WS_2 in vacuum.

4. Effects of environment on friction coefficient of composite film

Figures 3 and 4 shows the friction coefficient and surface component of wear traces for disk sample obtained by the friction test of composite films. As shown in Figure 3 (a), from a friction coefficient about 0.08 in vacuum, it increased to about 0.19 in air. Then it decreased to about 0.13 on the successive test in vacuum. This value of 0.13 in vacuum, however, is a little higher than that one obtained in vacuum only. And then it again increased to about 0.19 in the following test in air.

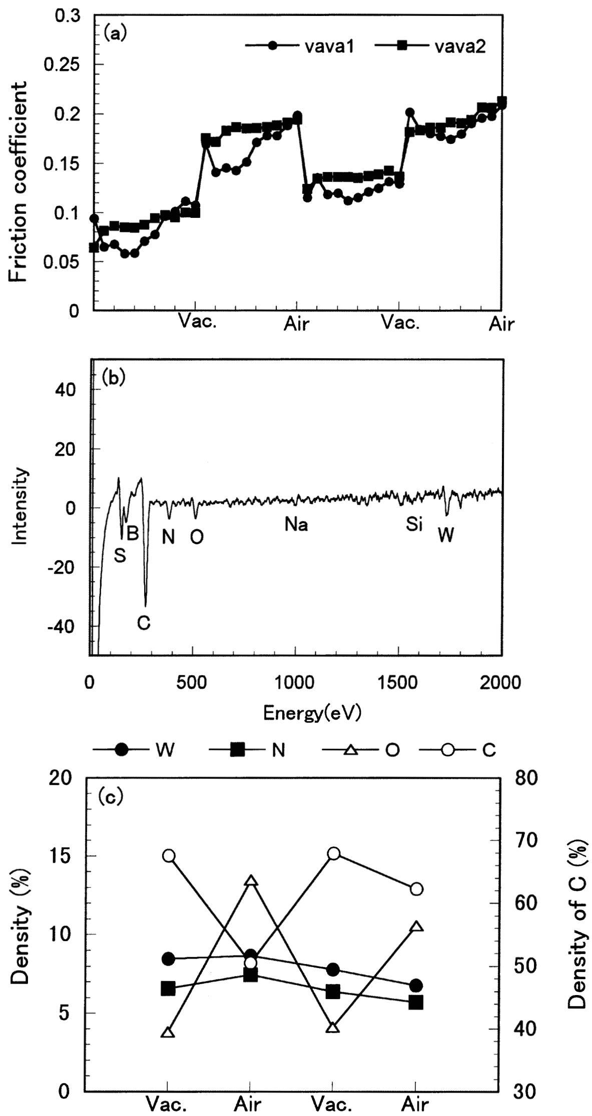

Fig. 3

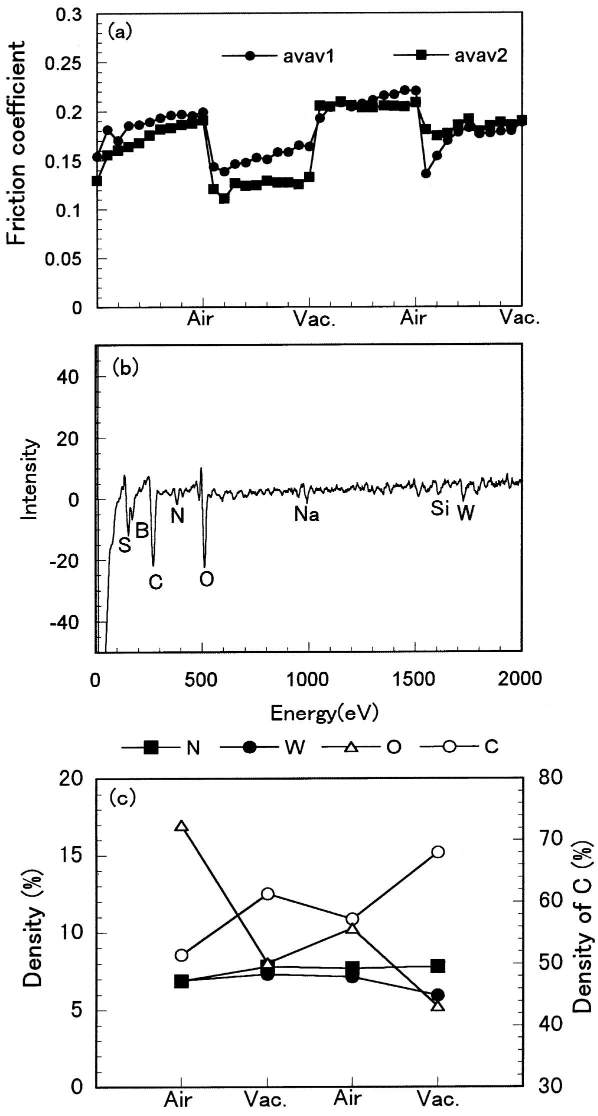

Fig. 4

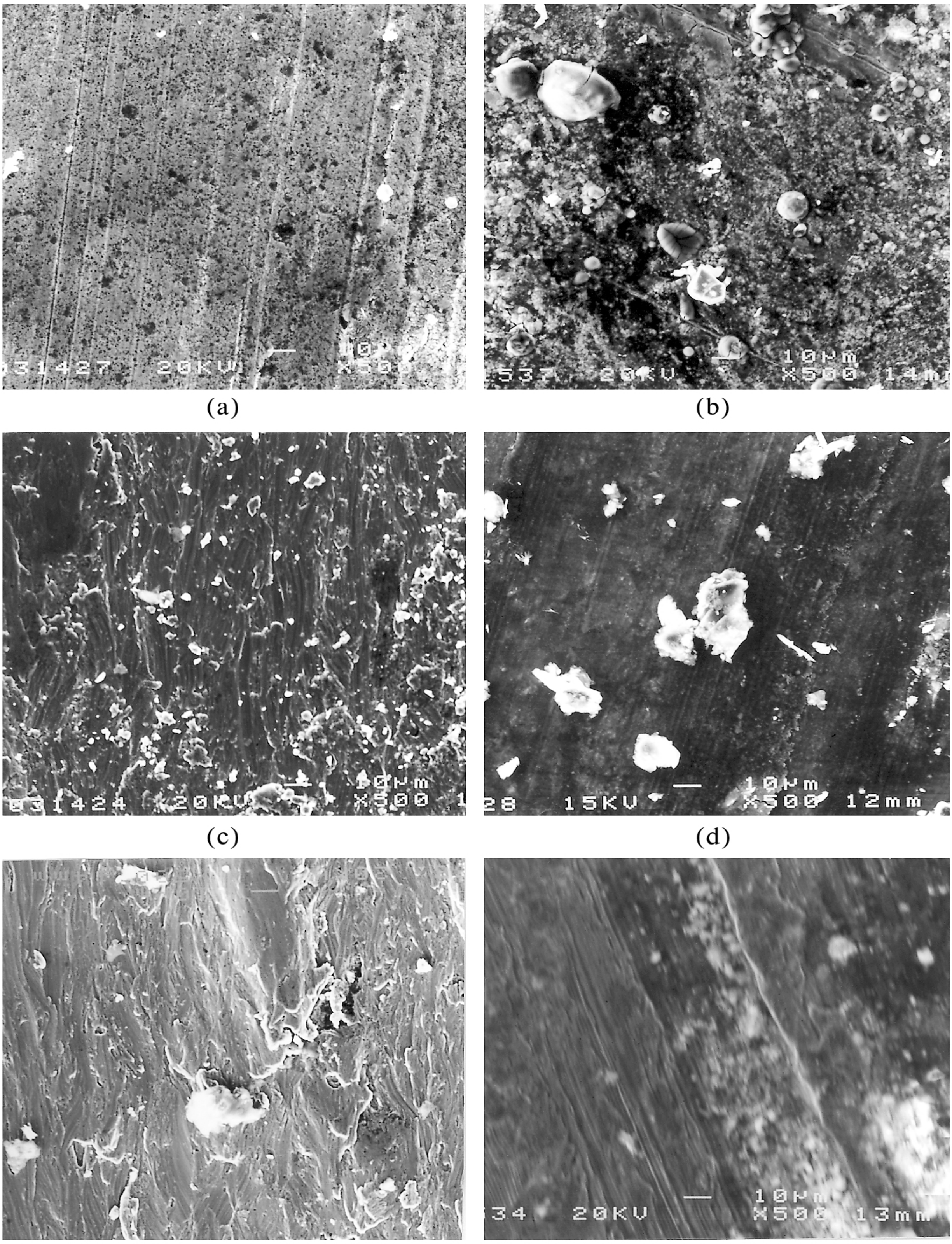
20KV
(a)
10µm
20KV
X500
(b)
10µm
20KV
X500
(c)
15KV
10µm
X500 12mm
(d)
(e)
20KV
10µm
X500
13mm
(f)

Fig. 5

Figure 3 (b), (c) shows the AES spectra and the results of quantitative analysis with relative inverse sensitivity for wear trace on various environments. Because the signals Na and Si are fuzzy like background, and the interference between the signals of S and B makes the amounts of these atoms unclear, the signals of N, C, and W show that all kinds of lubricants BN, graphite and WS_2. The density of oxygen and carbon were affected strongly by environment and it is interesting that the density of carbon was higher on the sliding surface tested in vacuum than that tested in air.

Figure 4 shows the results obtained by the friction test beginning in air. The changing tendency of friction coefficient and the density of oxygen and carbon on the wear trace are similar to that shown in Figure 3. The friction coefficient in vacuum also increases after the test in air, and the density of carbon increases after friction test in vacuum.

5. Sliding surface of composite films

Figure 5 shows typical topographic features of wear traces, which were taken from the individual film after friction test shown in Figure 2 (a), (b), (c). Only wear traces for WS_2 sliding in vacuum and graphite sliding in air formed tenacious films as shown in Figure 5 (a), (d), which prevent gross metal contact and provide long endurance life. The wear trace for WS_2 sliding in air is patch and has some cracks as shown in Figure 5 (b). The wear traces for graphite sliding in vacuum and BN in both environments are very rough as shown in Figure 5 (c), (e), (f), which present the metal to metal contact due to partial or complete removal of lubricant film.

Figure 6 shows typical topographic features of wear traces, which were taken from the composite films after the friction tests

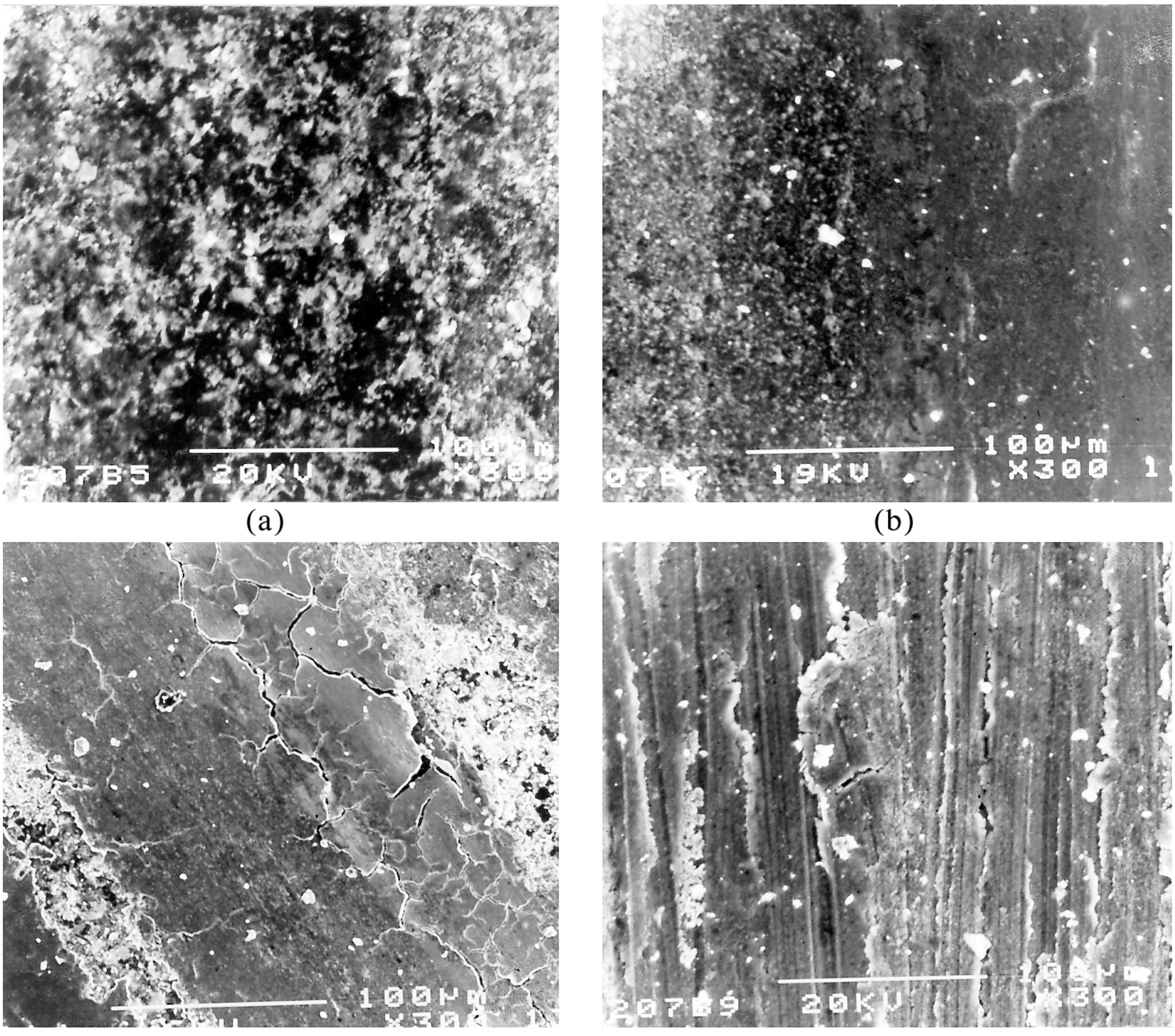

Fig. 6

shown in Figure 3, 4. Figure 6 (a) shows the wear trace of composite film after testing in vacuum only. This sliding surface is rough and looks like it's made from the cluster of powder. Figure 6 (b) shows the wear trace, which has undergone friction test in vacuum, air, vacuum, air. Though the friction coefficient of this film was higher than that of the film tested only in vacuum, the sliding surface is quite smooth. This result means that the surface roughness of wear trace is not directly related with its friction coefficient. Figure 6 (c) shows the wear trace of composite film after testing only in air. Though some cracks can be seen on the sliding surface, the greater part of sliding area is smoother than the one sliding only in vacuum. Figure 6 (d) shows the wear trace, which has undergone friction test in air, vacuum, air, vacuum. The sliding surface is smooth in comparison with the wear trace obtained by test in vacuum only. But it is rougher than the sliding surface obtained by the friction in air, while the friction coefficient is high.

6. Sliding surface of steel balls

Figure 7 shows the AES spectra for adhesive films on steel ball after sliding in air and in vacuum. It can be seen that tungsten disulphide, boron nitride and graphite adhere to the surface of steel balls both in vacuum and air atmosphere, which can prevent metal contact and get low friction coefficient and long endurance life for composite film. The high intensity of W atom means that the WS2 film mainly transferred on the surface of steel ball in vacuum as shown in Figure 7 (a). Comparing with Figure 7 (a), the intensity of Fe increased and W decreased as shown in Figure 7 (b). The high intensity of Fe means that the thickness of lubricant film transferred on the sliding surface of ball is thin. The low intensity of W means that does not only WS_2 plays an important role in air.

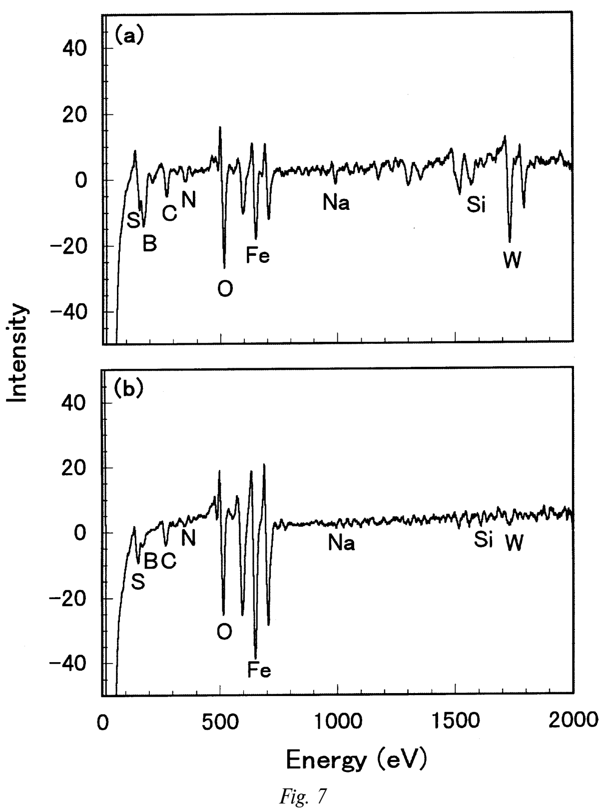

Fig. 7

7. Discussion

It is widely accepted that a good lubricant must have two important characteristics, shearing and adhering. Shearing can provide low friction, which is often explained by the basal-slip on intrinsic cleavage mechanism for lamella solid lubricants. For graphite and BN the adsorbed gases are responsible for the low friction, because the basal face of graphite has a low surface energy, the edges are highly active and react with gases and water in air, which decrease the surface energy of edges allowing sliding on basal face [13 - 18]. On the other hand, MoS_2 and WS_2 provide low friction in vacuum, and dry environment, because in humid environments the MoS_2 or WS_2 react with the oxygen or water and promote corrosion of metals by forming layers of oxysulphide according to following reaction [19]:

$$2WS_2 + 7O_2 + 2H_2O \rightarrow 2WO_2 \cdot SO_2 + 2H_2SO_4$$

$$2WS_2 + 7O_2 \rightarrow 2WO_3 + 4SO_2$$

In vacuum graphite exhibits a relatively high friction coefficient, in air the friction coefficient drops to 0.2, however, in contrast to graphite, the friction characteristics of WS_2 improve in vacuum as shown in Figure 2.

Adhering can provide long endurance life, because effective lubrication of metal surfaces depends on the existence of a layer lubricant, which prevents gross metal contact [20]. For this reason, BN is not a good lubricant either in vacuum or in air. Its adherence to the surface of steel ball to be lubricated is poor.

It is suggested that bonded with sodium silicate the lubricant powders were dispersed in composite film. Under the effect of perpendicular and shear forces, mica deformed and oriented nearly parallel to the surface of friction and lubricants were sheared [21]. In case of vacuum, WS_2 easy shear and easy form transfer film on the steel ball. WS_2 layer will attain low friction coefficient and low wear rate. Graphite and BN may be considered as unoriented polycrystalline mass for which the face-edge interaction is important [22]. Furthermore graphite debris piled up in front of steel ball. With the sliding the piled up graphite debris were pressured onto the wear trace of composite film. For this reason the wear trace of disk looks like a cluster of powder (Figure 6 (a)) and remains a lager of C (Figure 3 (c)). It is possible that graphite and BN powder decreased the real contact area where WS_2 is lubricating in vacuum. This may be the reason why composite film showed lower friction coefficient than WS_2 film only. By contrast, because WS_2 and graphite have nearly the same friction coefficients in air, both WS_2 and graphite shear in friction test. But WS_2 easily reacts with moisture and oxygen in surrounding environment to form WO_3 and sulphur compounds. The adherence to the steel ball is not good as in vacuum. With the increasing of friction force, the shearing not only takes place in the surface layer of graphite and WS_2, but also conduct mica to deform and let sodium silicate fracture. For this reason, the wear trace of disk looks smoothly and some cracks can be seen on wear trace of disk in air. Because WS_2 covered only the real contact area and the other area of graphite powder was laid uncovered, the concentration of C on wear trace was lower than that tested in vacuum where only WS_2 sheared.

Where the test was carried out in vacuum after in air, the friction coefficient was a little higher than the obtained by the test in vacuum only as shown in Figure 3 (a). In this case as graphite, WS_2, and BN shear together, and high forces of shearing let sodium silicate break down. The sodium silicate debris may become obstacle of the shearing of WS_2.

The endurance life of the composite film was similar to WS_2 film in vacuum and to graphite film in air. This is also explained as the friction of composite film was governed by the shearing of WS_2 in vacuum and by the shearing of graphite in air.

8. Conclusions

1. It is observed that the graphite, WS_2 and BN composite film showed the friction behavior, which resembles WS_2 and graphite in vacuum or in air respectively.
2. In changing from air to vacuum or from vacuum to air conditions, the composite film showed better friction behavior in vacuum than in air.

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10. References

[1] WINER, W. O.: Molybdenum disulphide as a lubricant: a review of the fundamental knowledge, Wear, vol. 10, pp. 422-452, (1967).
[2] GRATTAN, P. A., LANCASTER, J. K.: Abrasion by lamellar solid lubricants, Wear, vol. 10, pp. 453-468, (1967).
[3] RABINOWICZ, E., IMAI, M.: Frictional properties of pyrolitic boron nitride and graphite, Wear, vol. 7, pp. 298-300, (1964).
[4] BAHUM, C. J., JONES, J.R. : Influence of load, speed, and coating thickness on the wear life of a bonded solid lubricant, Lubr. Eng., vol. 25, pp. 351-361, (1969).
[5] SALOMON, G., DeGEE, A. W. J., ZEAT, J. H.: Mechano-chemical factors in MoS_2-film lubrication, Wear, vol. 7, pp.87-101, (1964).
[6] GARDOS, M. N.: The synergistic effects of graphite on the friction and wear of MoS_2 films in air, Trib. Trans., vol. 31, pp. 241-227, (1988).
[7] MARTIN, J. M., MOGNE, T. L., CHASSAGNETTE, C., GARDOS, M.N.: Friction of hexagonal boron nitride in various environments, Trib. Trans., vol. 35, pp. 462-472, (1992).
[8] SPALVINS, T.: Tribological properties of sputtered MoS_2 films in relation to film morphology, Thin Solid Films, vol. 73, pp. 291-297, (1980).
[9] LUI, J. J., ZHU, B. L., ZHANG, X. H.: The study of wear-resistance and microstructure of Pb-Sn-Ni brush plating layer, Wear, vol. 155, pp. 63-69, (1992).
[10] DONALD, H. B.: Friction and transfer behavior of pyrolitic boron nitride in contact with various metals, ASLE. Trans., vol. 21, pp. 118-124, (1978).
[11] ROWE, G. W.: Some observations on the frictional behavior of boron nitride and graphite, Wear, vol. 3, pp. 274-285, (1960).
[12] PRITCHARD, F., MIDGELEY, J.W.: The effect of humidity on the friction and life of unbounded molybdenum disulfide film, Wear, vol. 3, pp. 39-51, (1960).
[13] LIPP, L. C.: Solid lubricants-their advantages and limitations, Lubr. Eng., vol. 32, pp. 574-584, (1976).
[14] BARRY, H. F.: Factors relation to the performance of MoS_2 as a lubricant, Lubr. Eng., vol. 33, pp.475-480, (1977).
[15] TAKAHASHI, N.: Direct resolution of the layer lattice of molybdenum disulphide by transmission electron microscopy in relation to lubrication, Wear, vol. 124, pp. 279-289, (1988).
[16] BARTZ, J.W.: Describing wear life of bonded solid lubricants by laboratory methods, Lubr. Eng., vol. 41, pp. 607-612, (1985).
[17] GRATTAN, P. A., LANCASTER, J. K.: Abrasion by lamellar solid lubricants, Wear, vol. 10, pp. 453-468, (1967).
[18] NISHIMURA, M.: The introduction of solid lubrication,(in Japan) Science of Machine, vol. 37, pp. 305-310, (1985).
[19] BHUSHAN, B., GUPTA, B. K.: Handbook of tribology, McGraw-Hill Publishing Com. Press, New York, 1991.
[20] BUCKLEY, D. H.: Surface effects in adhesion, friction, wear and lubrication, trib. ser. 5., Elsevier Scientific Publishing Com. Press, Amsterdam, 1981.
[21] LI, C. S., SEKIGUCHI, S., ASAI, Y., TSUYA, Y., UEMURA, M.: The high temperature tribological behavior of WS_2 inorganic bonded film, Japanese Jour. Trib., vol. 34, pp 50-57, (1998).
[22] DEACON, R. F., GOODMAN, J. F.: Lubrication by lamellar solids, Proc. Roy. Soc., in London, vol. 243, pp. 464-482, (1958).