Surface modification by tribochemical treatment in-situ

Da-Chang Du*, Seock-Sam Kim, and Chang-Min Suh
School of Mechanical Engineering, Kyungpook National University,
1370, Sankyuk-Dong, Puk-Ku, Taegu 702-701, Republic of Korea

Abstract

Tribological conditions and additive chemistry between frictional interfaces were discussed in the present paper. The principles of the tribochemical surface modification were drawn on the basis of data of literatures and experiments. Results of gear tests proved experimentally that the principles would have potential applications in industry.

Keywords: surface modification, tribochemistry, deposit film, permeation film, antiwear additive

1. Introduction

Modern technologies, such as heat treatment, chemical heat treatment, CVD, PVD, electronic deposit, thermal spray, ion implantation, laser surface treatment, and etc., have extremely improved surface properties of materials. However, these technologies are always used to machine parts just before assembly. It is well known that the parts will not be coupled very well owing to metal-working and assembly errors and material deformation; so a running-in process must be involved. As such, the surface modification layer will be thinned during the running-in process; and the modification layer will be worn down and finally worn out during its service. This is the pre-modification method for machinery. Although the pre-modification is very important for surface engineering, what can we do much better for machine? It is possible that on-line surface modification for machine parts should be able to compensate above defects. Apparently, we cannot use any other measurements to reach the on-line surface modification technology but the lubricants that reach and lubricate any frictional surfaces at any time during its service. Therefore, lubricant chemistry and tribochemistry are vital for this purpose.

In the present paper, we will discuss additive chemistry and report the effectiveness of surface modification by tribochemical treatment in situ in gear system during friction.

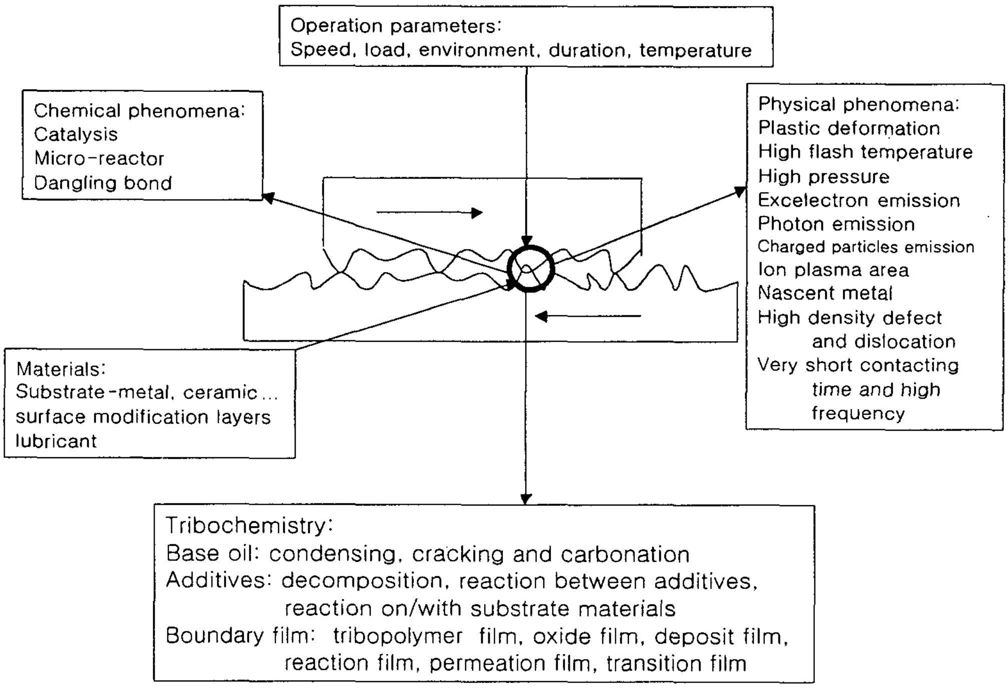


Fig. 1. Schematic illustration of tribological conditions

Table 1. Elemental periodic table

IA	IIA											IIIA	IVA	VA	VIA	VIIA
Li	Be											**B**	**C**	N	**O**	**F**
Na	**Mg**	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	Al	**Si**	**P**	**S**	**Cl**
K	**Ca**	Sc	**Ti**	V	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	Ga	Ge	As	**Se**	**Br**
Rb	Sr	Y	Zr	**Nb**	**Mo**	Tc	Ru	Rh	Pd	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**
Cs	**Ba**	**La**	Hf	Ta	**W**	Re	Os	Ir	Pt	Au	Hg	Tl	**Pb**	**Bi**	Po	At

2. Principles of tribochemical surface modification

2.1. Conditions in friction interface

A typical tribological system can be described schematically as shown in figure 1. This system is so complicated that it is always called as a black box . Every component is of an important element contributed to the performance of the whole tribology system.

2.2. Additive chemistry and EP additives

2.2.1 Functional groups in antiwear

In additive chemistry, the most important is functional groups of the additive molecules. Most of the elemens in additives are the capitalized elements in the Periodic Table 1. Actually, for an organic additive, the elemental carbon is not only the carrier for oil-solubility, but also very important group for additive properties, to some extent, it will significantly influence on their tribological performances of the model compounds due to different chemical structures, chemical functional groups and molecular weight.

(1) Non- and semi-metal elements

Non-metal elements with high electronegativity may exhibit good tribological performance through competitive absorption on the rubbing surface. For example, F-containing synthetic oils exhibit excellent tribological properties [1], and some inorganic compounds, e.g., CaF2, LiF, and BaF2, are good solid lubricants [2].

Elemental oxygen always exists in carboxyl, ether, ester and ethanol, which have strong polarity. These compounds can take action by means of friction polymerization during rubbing [3]. Sometimes elemental nitrogen takes positive action and sometimes takes negative action in terms of tribological property. For example, the detergent succinimide added into ZnDTP-containing oil resulted in an antagonistic effect for tribological properties [4]. Elemental nitrogen can change the components on the rubbed surface, in which the amount of sulfides was reduced and the amount of oxides was increased through hindering the antiwear action of ZnDDP.

Sulfur, phosphorus, and chlorine are the main functional elements for antiwear additives used in lubricants among non-metal elements. Most of antiwear and EP additives are derived from these elements. And they are described in detail in the literature [5]. Common organic groups are dithiophosphate, dithiophosphite, dithiocarbamate, phosphate, phosphite, mercaptan, disulfide, sulfur ether, chlorinized paraffin, and other chlorine-substituting organic compounds. Different alkyl groups also influence tribological performances of their compounds significantly [6,7].

In the Group VIIA, elemental S, Se, and Te have the decreasing ionicity as the sequence, which causes the molybdenum disulfides have the most ionic with the sequence of $MoS_2 > MoSe_2 > MoTe_2$, which further results in the tribological performance with the same sequence [8].

The elemental boron has many special characteristics. It has very small atomic radius that can make itself be an element for intermetallic compounds. The elemental boron in its compounds always is at electron-lacking state that results in the compounds not being stable, especially easy to be hydrolyzed [9]. It may become an extremely potential substitute element for some weight metal elements that are harmful to health and environment [10].

(2) Metal elements

Most of metals are functional elements in both organic and inorganic compounds for anti-wear and friction reducing purposes. In the Groups IA and IIA, due to their strong ionicity, they tend to form ionic compound, as such, the compounds containing these elements have strong basicity. Factually, they are always used for dispersants, e.g., calcium and magnesium sulfonates used in engine oils.

In the Groups IIIA, IVA and VA, elemental Sn, Sb, Bi, Pb and In are soft metal and become self-lubricating materials [5] and these elements are easy to be reduced during friction. They can act as elements of soft metal deposited film.

In the transition elements, the potential elements can be categorized as three parts: the first is those which can react with elemental sulfur and produce metal sulfides with layer structures, such as Mo, W, and Nb; the second is those which can be deposited as soft metal film, such as Ag, Cu, and Ni; and the last is those which can be formed as metal oxides, such as Ti, V, Cr, Ni, Mn, Zn, and Cd.

Rare earth elements become more and more interesting, both of inorganic [11] and organic [12] compounds.

Organic groups also affect on the tribological properties of those organometal compounds with the same metal element [6,7]. Adversely, metal elements also affect on the tribological behaviors of those organometal compounds with the same organic group, for example, different metals in the metals dithiophosphate (MDDPs) exhibit different antiwear and EP properties [13,14].

2.2.2. Boundary lubrication film

2.2.2.1. Sacrificed film

It is well accepted that elemental sulfur and chlorine can reacted with iron substrate to form soft modification layer with lower shear stress. The lower shear stress film can reduce friction coefficient and keep the metal from scuffing, but its wear resistance is sacrificed, which results in the service life of the machine parts being decreased. Although surface films are complicated and will be changed as testing conditions, the basic components in the boundary films are as follows: As sulfur-containing agents are used in lubricating oil, FeS, FeS_2 and $FeSO_4$ are common species in the rubbed surface [15]; phosphates, phosphites and phosphides can be detected in the worn scars when organophosphorus compounds are employed [16]; $FeCl_2$ is the main species in the rubbed surface as chlorine-containing compounds are involved [17]. Their load-carrying capacities are related to their chemical reactivity [18].

2.2.2.2. Non-sacrificed film

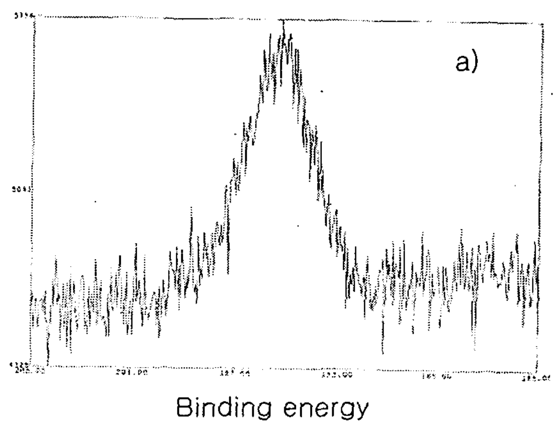
2.2.2.2.1. Formation of permeation layer

(1) Boronization

Boron-containing compounds including organic and inorganic used as antiwear additives have been studied. Adams considered boron-containing species as potential additives in 1980s [19]. Gear oil formulated with boron-containing compounds exhibits excellent antiwear performance and oxidation resistance in contrast with general sulfur- and phosphorus-based gear oil [20,21]. Dong et al [22] reported that boron-containing additive was decomposed during friction, and then formed boron oxides on the rubbed surface under mild load and produced FexBy species in the worn surface under wild load.

In the case of tripropanol borate as a model additive, tested in a four-ball tester, results of XPS analysis on the rubbed surfaces showed that the elemental boron existed as different chemical species under different loads (see figures 2, 3 and 4). The elemental boron existed as organic borate (195eV) in the rubbed surface under a mild load (300N). There existed boron oxide and boric acid (192.5-194eV) in the outer surface under the loads of 600N and 1000N. After sputtered for 5min and 10min, it is shown that the XPS peaks shift towards lower binding energies. In these cases, it has been detected that Fe2B (188.5 eV) existed in the subsurface and FeB (188 eV) in the inner surface.

In chemical heat treatment, boronization is a common measure for improving wear resistance, in which both of Fe_2B and FeB are basic physical phases. Thus, under severe conditions, the boron-containing compound can happen to decompose and produce atomic boron to permeate into subsurface to strengthen surface tribological properties in situ. Similar results also have been confirmed as nanoparticle inorganic borates were used as antiwear additives in lubricating oils [23].



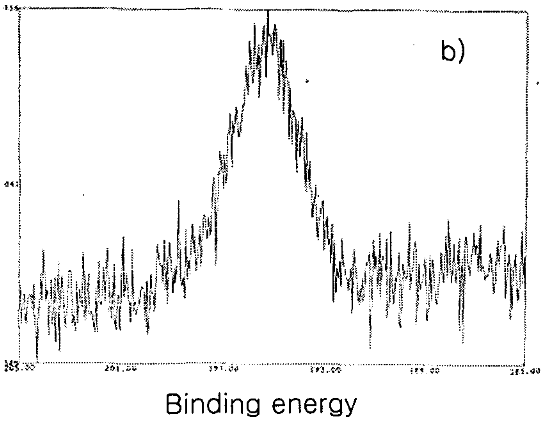
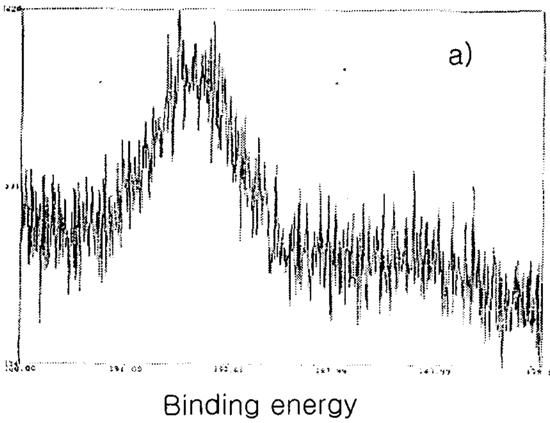


Fig. 2. B1s spectra for $C_9H_{21}BO_3$ 15%, 300N, 10min, 1450rpm, 4-ball tester

a) Surface, spt-0min; b) spt-5min



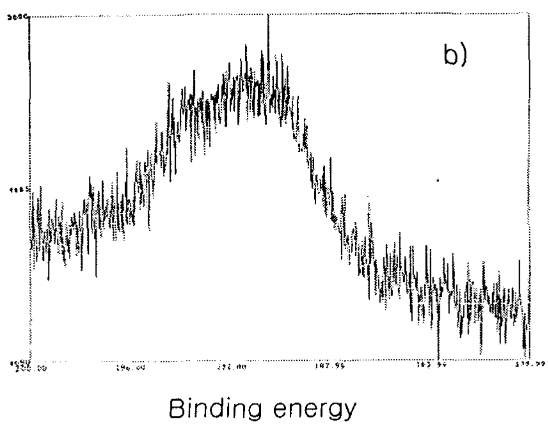
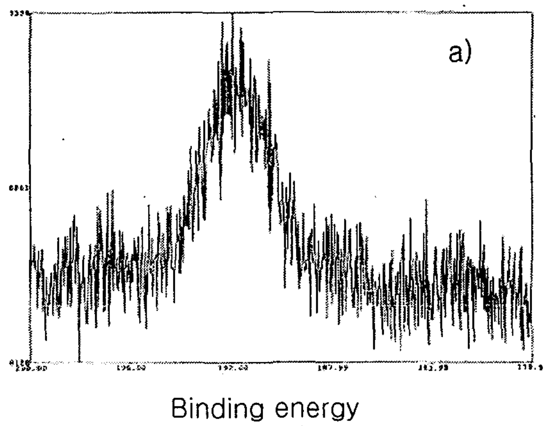
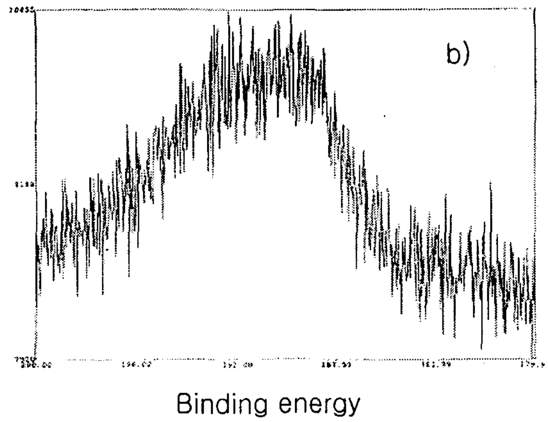


Fig. 3. B1s spectra for $C_9H_{21}BO_3$ 15%, 600N, 10min, 1450rpm, 4-ball tester

a) Surface, spt-0min; b) spt-5min





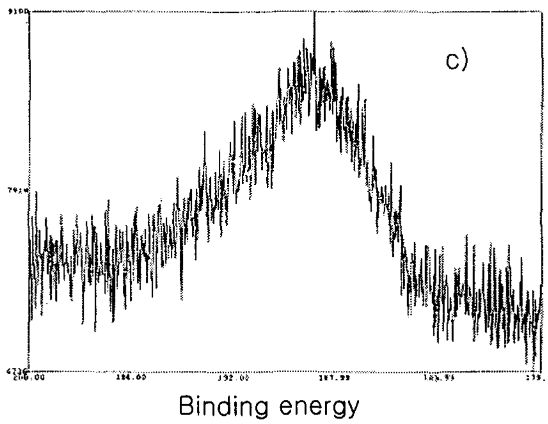


Fig. 4. B1s spectra for $C_9H_{21}BO_3$ 15%, 1000N, 10min, 1450rpm, 4-ball tester

a) Surface, spt-0min; b) spt-5min c) spt-20min

(2) La promotes the permeation of boron

In chemical heat treatment, it is well known that rare earth elements can promote other elements to permeate into metals. So a rare earth elemental La-containing additive was employed to mix with the model borate in lubricating oil for friction and wear testing. XPS spectra are shown in figure 5. The spectra indicate that B1s binding energy on the surface locates at around 188 eV with a broad peak, which should belong to Fe2B and FeB species. After sputtered, two peaks appeared at around 194 eV and 187 eV, which should be contributed to boric acid and B_4C, respectively.

In contrast with those of species in rubbed surfaces as borate was used alone, the intensities of Fe_2B and FeB in XPS spectra are much stronger in this binary system. This is resulted from the La-containing additive being added. The rare earth elemental La promoted atomic boron to be created and permeate into substrate. The results of AES analyses of the rubbed surfaces (see AES spectra in Fig.6) also confirmed the above hypothesis. During the sputtering time, in the cases of borate used alone, atomic concentrations of boron are between 15-3% under the load of 800N and 12-5% under the load of 1000N; in the cases of the mixtures, they are between 25-12% under the load of 800N, 35-15% under the load of 1000N, and 29-15% under the load of 1250N. Thus, there are much higher concentrations in rubbed surfaces after the rare earth additive was added.

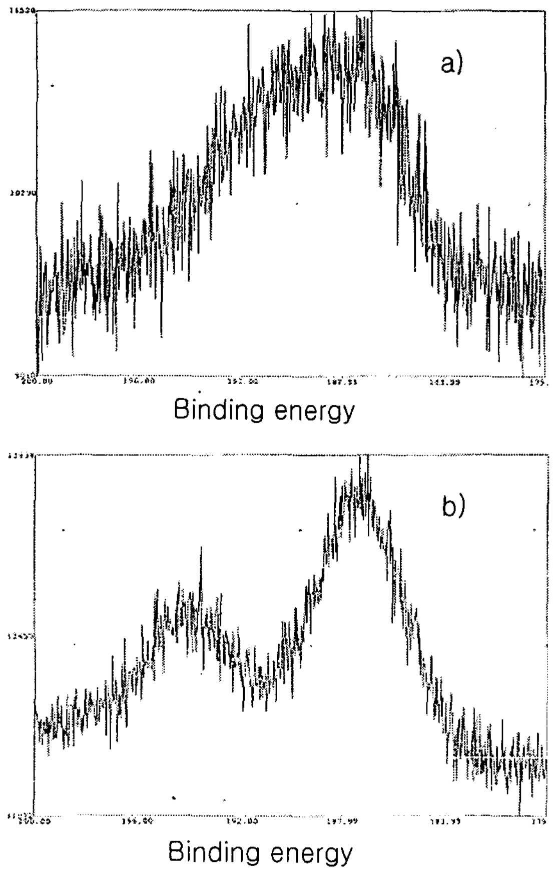
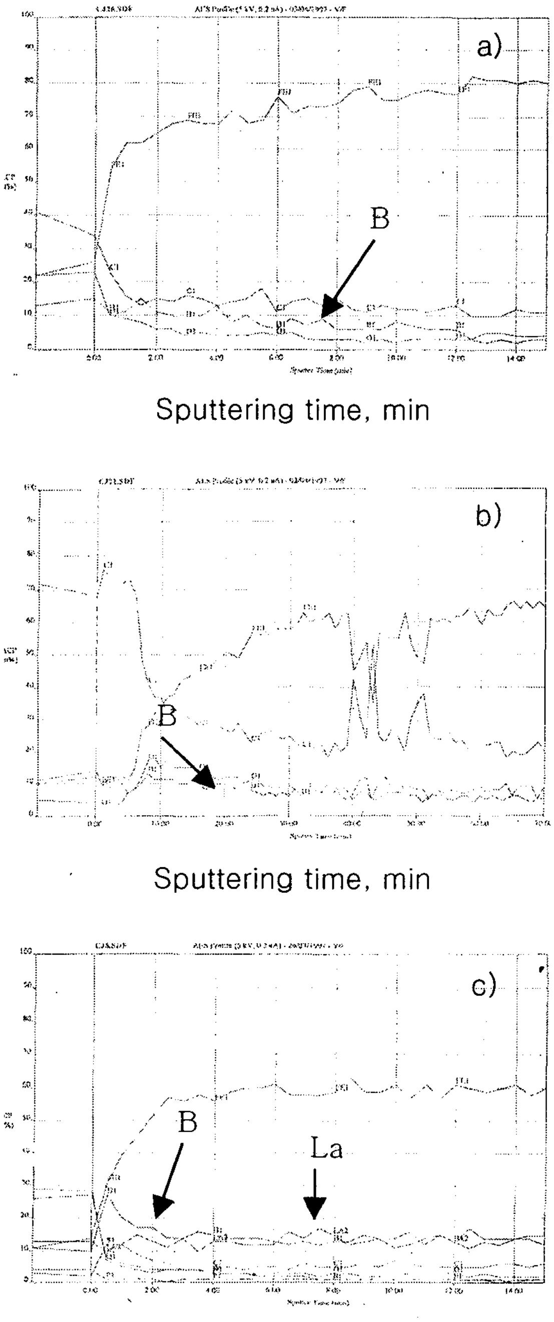


Fig. 5. B1s spectra for $C_9H_{21}BO_3$ 15% + LaDDP15%, 1000N, 10min, 1450rpm, 4-ball tester

a) Surface, sputtring 0min; b) sputtering 2.5min



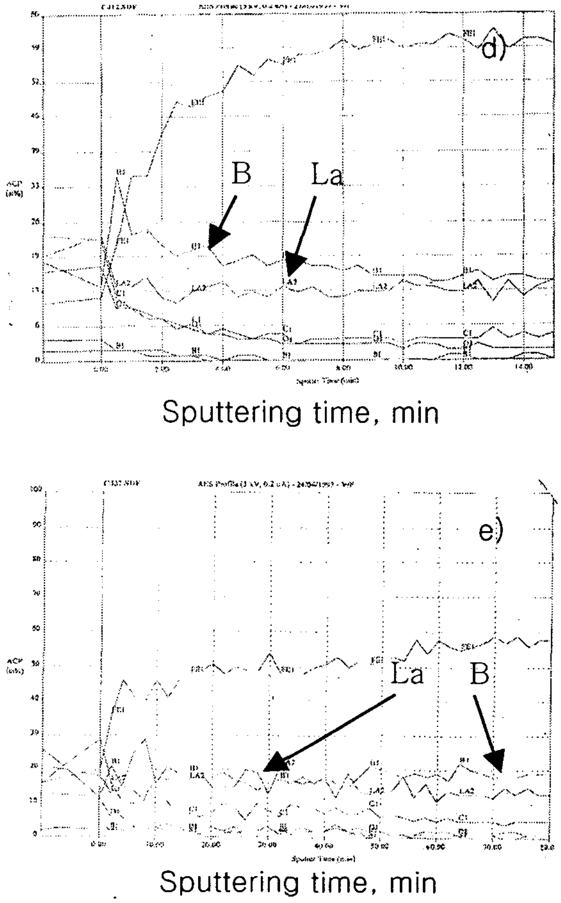


Fig. 6. AES spectra: 10min, 1450rpm, 4-ball tester.

a) $C_9H_{21}BO_3$ 15%, 800N, b) $C_9H_{21}BO_3$ 15%, 1000N, c) B15%+La15%, 800N; d) B15%+La15%, 1000N, e) B15%+La15%, 1250N

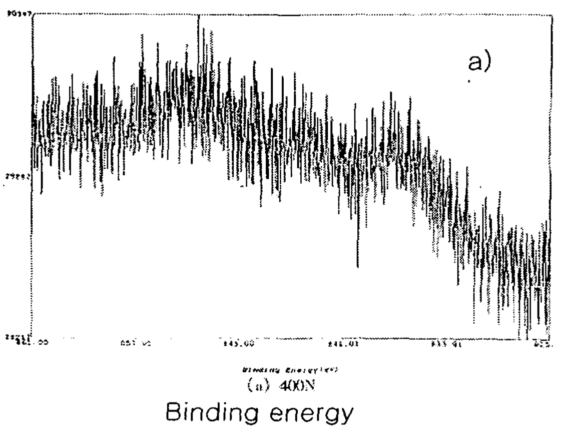
2.2.2.2.2. Deposit film

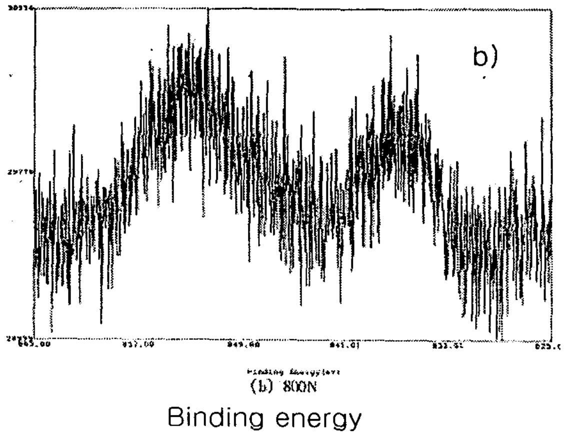
(1) Soft metal film

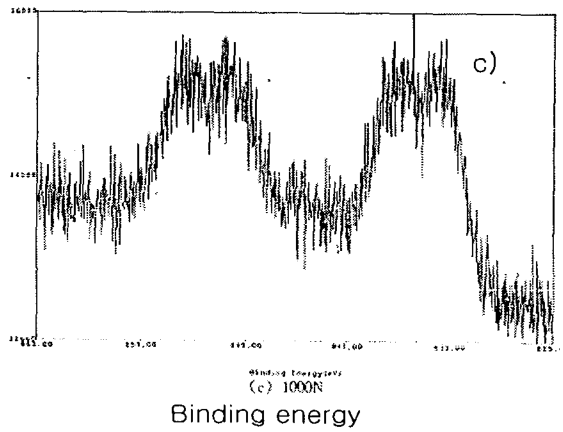
Elemental copper can be deposited on rubbed surface from copper-containing additives in lubricating oil during friction, which has been observed by XPS analysis [24]. On the basis of the deposited copper film, a self-repairing concept has been developed for some industrial applications, which focuses on repairing scratched surfaces by means of copper being deposited in-situ during friction.

Similar to copper-based additives, tin-based additives can also be deposited on the worn surface during friction. And this process can be speeded up by organic borate [25].

For the mentioned La-based additive, species in the worn scares have been analyzed by XPS. The results are shown in figures 7 and 8. The figure 7 indicates that relatively weak peaks appear, which belongs to La oxides (c.a. 835eV) under mild loads (400N and 800N); two separated XPS peaks appear under wild loads (1000N and 1250N), which are contributed to atomic La (ca. 836eV) and La oxides (ca. 834eV). Results of AES analysis (Fig. 8) further confirmed the deposited films are very thick, even reached the atomic concentration of 45% in worn surface (1250N).







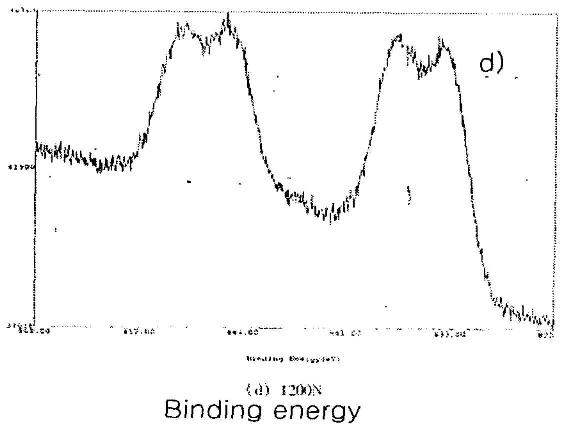


Fig. 6. La3d XPS spectra, LaDDP 20%, 10min, 1450rpm, 4-ball tester

400N; b) 800N; c) 100N; d) 1200N

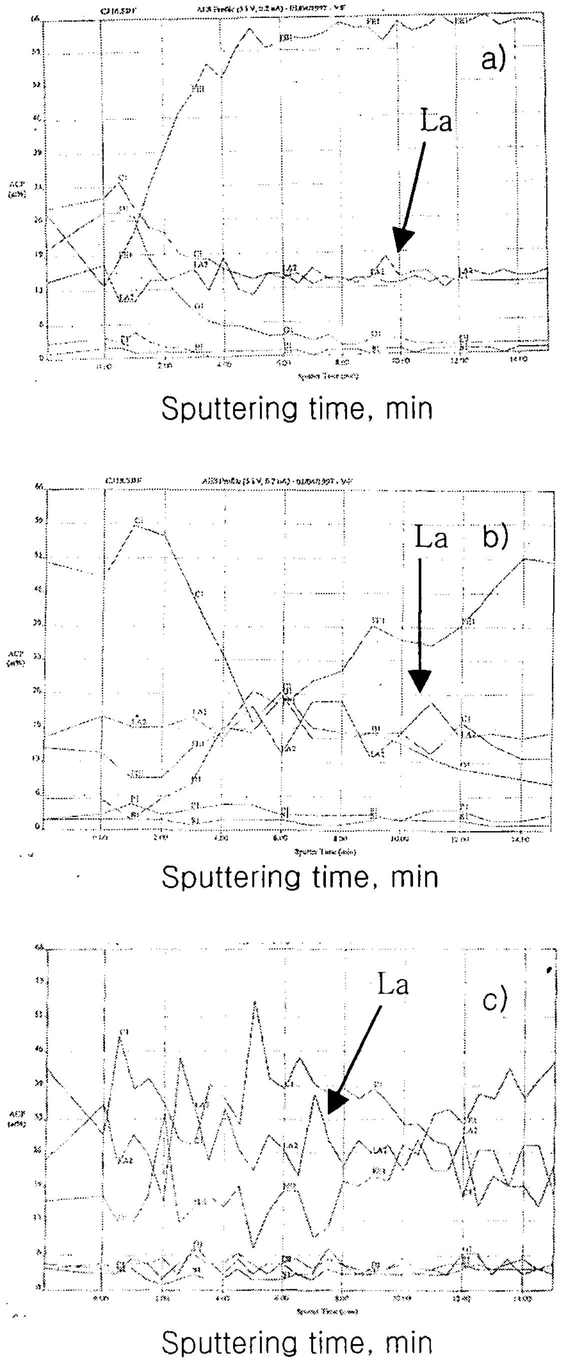


Fig. 8. AES spectra: LaDDP 20%, 10min, 1450rpm, 4-ball tester

a) 800N; b) 1000N; c) 1200N

(2) Graphitization on surface

In-situ formation of solid lubricants have been reported by many researchers, e.g., deposited carbon film from gaseous materials [26] and from ether and ester base lubricants [27]. Interestingly, under a temperature of 450℃, graphite-like carbon film with excellent tribological behaviors under high temperature can be produced from a mixed ether oil on a molybdenum alloy during rubbing and have been characterized by XPS and Raman spectra [27].

(3) MoS_2

MoS_2 is also an important tribochemical reaction product. Molecules containing elemental Mo and S can be decomposed and produce MoS_2 on the rubbed surface, for example, MoDTC [28] and MoDDP [29].

Elemental Mo in Mo alloy can react with elemental sulfur in ZnDDP in lubricating oil and form MoS_2 during friction [27]. Ion-implanted Mo in the iron substrate also reacts with elemental sulfur from ZnDDP during [30] and MoS2-like species can be formed on worn surfaces in situ.

2.2.2.2.3. Other solid lubricants under high temperature

The composite of tungsten disulfide nanocrystalline ZnO films exhibited excellent tribological behaviors in the range of room temperature up to 500℃. Surface analysis indicated that zinc tungstate ($ZnWO_4$) had been formed in situ in the rubbed surface at the temperature of 500℃ [31].

3. Application of tribochemical treatment in gear

An application of tribochemical treatment in gear has been involved using a standard FZG gear test rig. The material of gear is 40Cr. The process of the tribochemical treatment is as follows:

Parameters: Rotation speed: 1450rpm; load: grade 6; temperature: 120℃; running-in duration: 2.5 hrs; lubricants: 100% organoboron additive, 80% organoboron additive plus 20% La-containing additive and base oil 350N. During running-in procedure, the additives were employed as well as base oil as a comparison group. After running-in process, the gear system was cleaned by petroleum ether, and the base oil was employed again for study if the additives could improve the load-carrying capacity.

The results of gear tests are listed in Table 2. The gear loads related to the gear grade are listed in Table 3. From the results listed in Table 2, we can see the tribochemical treatment exhibit good tribological effect on gear load-carrying capacity, and the principle of tribochemical treatment has been confirmed.

4. Conclusions

(1) Additive chemistry needs much more attentions to be paid into molecular-tailored additives for the control of tribological property.

Test oil for running-in		Oil for gear load-carrying test	Gear test: (gear load-carrying grade)
Base oil	Additive		
350N	--	350N	5
--	Organoboron	350N	6
--	Organoboron+La-containing additive	350N	7

Load grade	1	2	3	4	5	6
Loads at unit length on gear surface	4924	20272	52144	89804	19052	199887
Load grade	7	8	9	10	11	12
Loads at unit length on gear surface	270861	353424	446125	550414	651806	789410

(2) Boron-containing additive can form FeB and Fe2B phases in the rubbed surface in-situ to improve surface tribological behaviors.

(3) La-containing additive can promote the elemental boron to permeate into substrate during friction like tribo-catalytic effect.

(4) Tribochemical treatment exhibits good surface modification effectiveness in gear system in this test.

Acknowledgement

The authors wish to express their thanks to Dr. Jiang for some experimental results.

Reference

1) T.W., Del Pesco, in Synthetic Lubricants and high-performance functional fluids, ed. By R.L., Shubkin, Marcel Dekker, Inc., New York, 1993. pp.145-172
2) H.E., Sliney, T.N., Strom, and G.P., Allen, ASLE Trans., 8(1965)307-322
3) Y.H., Hu and W.M., Liu, Wear, 218(1998)244-249
4) J.M., Martin, C.Grossiord, T.Le Mogne and J.Igarashi, Tribology International, 33(2000) 453-459
5) A. Dorinson and K.C. Ludema, Mechanics and Chemistry in Lubrication, Tribology series, 9, Elsevier, 1985
6) G.J.J., Jayne and J.S., Elliott, J. Inst. Petroleum, 56(1970)42-49
7) E.S., Forbes, Wear, 15(1970)87-96
8) M.N., Gardos, in New Directions in Tribology, ed. I.M., Hutchings, 1997, pp.229-250
9) J.B., Yao and J.X., Dong, Lubr. Eng. 51(1995) 475.
10) C., McFadden, C., Soto and N.D., Spencer, Tribology Inter., 30(1997)12, 881-888
11) Lu, Jinjun; Xue, Qunji, Tribology Transactions, 43(2000)1, 27-32
12) C. Boshui, D. Junxiu and C. Guoxu, Wear, 196(1996)1-2, 16-20
13) K.G., Allum and E.S., Forbes, Proc. Inst. Mech. Engrs., 183(1968/1969)Part 3P, 7-14
14) C.N., Rowe and J.J., Dickert, ASLE Trans., 10(1967) 85-90
15) A., Dorinson and V.E., Broman, ASLE Trans., 5(1962) 75-90
16) W.R., Pistillo and A.T., Riga, Tribology-solving Friction and wear problems: 10th international colloquium, ed. By W.J. Bartz. Jan. 1996
17) P. V. Kotvis, J. Lara, K. Surerus and W. T. Tysoe, Wear, 201(1996), 1-2, 10-14
18) T., Sakuai and K., Sato, ASLE Trans., 9(1966) 77-87
19) J.H., Admas, D., Godfrey, Lubrication Engineering, 37(1981),16
20) J.H., Admas, Lubr. Eng., 34(1978) 12
21) J.H., Admas, Lubr. Eng., 34(1977) 46
22) J. X., Dong, G. X., Chen, X. M., Luo, and L. G., Chen, Lubr. Eng., 50 (1994) 1, 17-22
23) Z.S. Hu, J.X. Dong, G.X. Chen, J.Z. He, Wear 243 (2000) 4347
24) J.B.,Yao, J.X.,Dong and R.G.,Xiong, Lubr. Eng, 50, (1994).9,695-698,

25) J. B. Yao and J. X. Dong, Lubr. Eng., 51, (1995). 3, 231-233,

26) J.L., Lauer and B.G., Bunting, Tribology Trans., 31(1988) 338-349

27) Y.S, Jin and C.H., Zhou, Wear, 205(1997) 77-87

28) C., Grossiord, K., Varlot, J.M., Martin, Th.Le, Mogne, C.Esnouf and K., Inoue, Tribology International, 31(1998)12, 737-743

29) C., Grossiord, J.M., Martin, Th.Le, Mogne, Th., Palermo, Tribology letters, 6(1999) 171-179

30) Q.J., Xue and M.W. Bai, Wear, 195(1996)66-73

31) S.V., Prasad, N.T., McDevitt and J.S. Zabinski, Wear, 237(2000) 186-196