

Tribochemical Mechanism of Borate of Triethanolamine in Water Solution by XPS

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 behaviors of a borate of triethanolamine in water solution were evaluated using a four-ball wear tester. X-ray photoelectron spectroscopy (XPS) was employed to study tribochemical species on worn scars of steel balls. Results show that a thick deposit layer was produced on the worn scars, which came from the decomposition of the borate. The surface film on the worn scars was mostly consisted with H_3BO_3 , B_2O_3 and large amounts of ferricyanides.

Key words : Borate, triethanolamine, tribochemistry, XPS

Introduction

As a kind of antiwear additive, boron-containing compounds have been used in lubricating oil. Tribochemical mechanisms of some boron-containing compounds in lubricating oil have been probed by different researchers. Dong etc [1] indicated that organic borate was decomposed and produced active atomic boron during friction, which permeated into thin surface layer and created Fe_xB_y compounds in situ with iron substrate. They further concluded that the action effects of the borate during friction were similar to those of chemical thermal treatment. Borates also could create boron oxide on rubbing surface under the mild working conditions [1,2]. Liu etc. [3,4] suggested that main species should be organic borates with low molecular weight, which just absorbed on the worn surface after tested. Owing to boron atoms empty orbit, borates can play a catalysis role in the existence of copper-containing organic compounds [5,6], rare earth elements-containing compounds during friction and promotes copper to deposit on the rubbing surface and rare earth elements to permeate into subsurface layer.

On the other hand, tribological behaviors of some inorganic borates have also been intensively investigated. Adams et al. [7] suggested that the inorganic potassium borate took its action through the formation of deposited film on worn surface by means of electrophoretic process. Boric acid is a very high efficient antiwear additive that should be contributed to its sandwich structure [8]. And boric acid is also widely used as antiwear and antirust additive in aqueous working fluid.

Triethanolamine (TEA) is a common industrial compound which is usually used to aqueous cutting fluid as an antirust agent. TEA with high base can react with organic acid such as oleic acid to produce some compounds with oiliness and surface activity. This reaction progresses through dewater

reaction between TEAs ethanol hydroxyl and acids carboxyl. As such, borate of TEA can also be obtained through dewater reaction of boric acid and TEA. Actually, this borate of TEA has been used to aqueous cutting fluid as antiwear and antirust additive with high properties in antiwear and antirust. However, few reports can be available on tribochemistry of boron-containing compound in water solution.

Experimental

The borate of triethanolamine was synthesized in terms of 2.5 : 1 mole ratio of boric acid and triethanolamine (TEA) at reaction temperature about 140°C for 40 minutes. The final reaction product is a clear and viscous fluid.

Tribological features were evaluated by using a four-ball tester. Ball with 12.7 mm in diameter was made of AISI-52100 steel. The test conditions were as follows: main axis rotation speed 1500 rpm, loads 98 N, 196 N, 294 N and test time 20min at room temperature. Concentrations of the borate were 100%, 10%, 5%, and 3% in de-ionized water.

An X-ray photoelectron spectroscopy (XPS) with Mg Ka target was employed to analyze chemical composition on the down balls worn surface after being tested under a load of 294 N for 20 min. Special attention has been paid to the photopeaks of Fe_{2p} , B_{1s} , N_{1s} and C_{1s} . Binding energies were referenced to the C_{1s} binding energy from carbon contamination (284.8 eV) to account for specimen charging.

Results and Discussions

Tribological tests

Tribological results are shown in Figure 1. Figure 1 indicates that the model compound exhibited good wear resistance. The wear resistance decreased with the decrease of the added concentrations of the model compound in water solution. Under the load of 196 N, the water solution could not stand the

[†]Corresponding author; E-mail: dcd@yaho.com

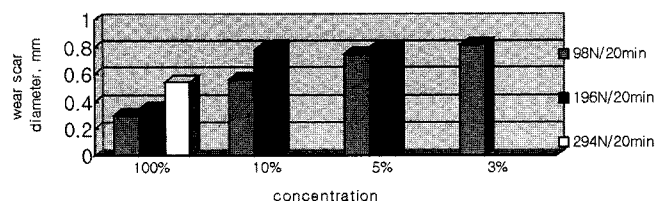


Fig. 1. Effect of the model's concentration on wear scar diameter.

test duration at the concentration of 3%. Under the load of 294 N, only pure additive can stand the test duration. Additive-free water could not stand such tests.

XPS analysis

After the water solution with a treating rate of 10% has been tested under the load of 294 N for 20 min, the worn surface films on the down balls were investigated by XPS. The XPS spectra of the main elements on the worn scars are shown in figures 2, 3, 4 and 5.

The changes of B_{1s} binding energies with sputtering time are shown in figure 2. Binding energy of B_{1s} on the outer worn surface located at around 193 eV with a right companion peak at about 192 eV. They belonged to H_3BO_3 and B_2O_3 , respectively [9]. The former was stronger than the latter. After the worn surface had been sputtered for 15 min, the main peak of B_{1s} moved to the location with a binding energy at around 192 eV, whereas the peak at 193 eV disappeared. Then continuing to have been sputtered for 20 min and 50 min, the binding energies of B_{1s} were not changed and still were at around 192 eV with stronger intensities. The stronger intensities, after having been sputtered for a long time,

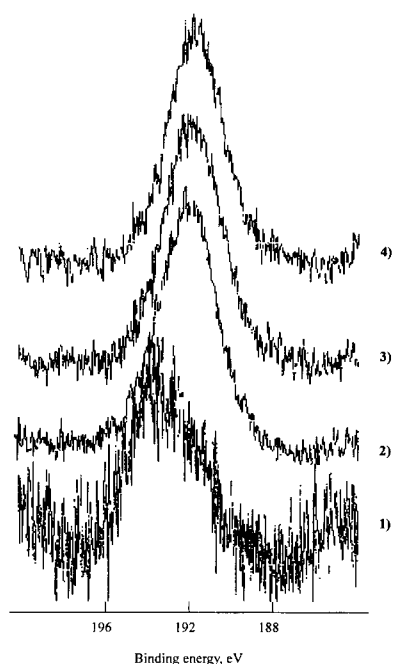


Fig. 2. B_{1s} spectra with sputtering time. 1) 0 min, 2) 15 min, 3) 35 min, and 4) 65 min.

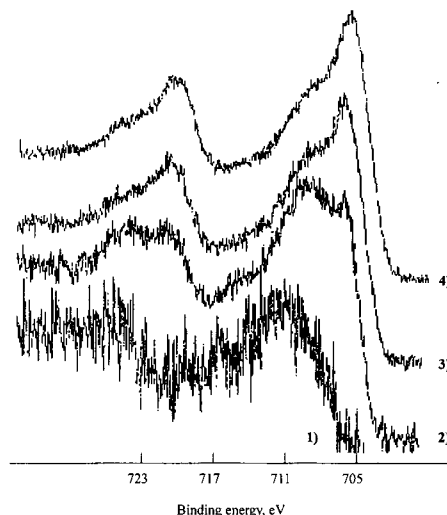


Fig. 3. Fe_{2p} spectra with sputtering time. 1) 0 min, 2) 15 min, 3) 35 min, and 4) 65 min.

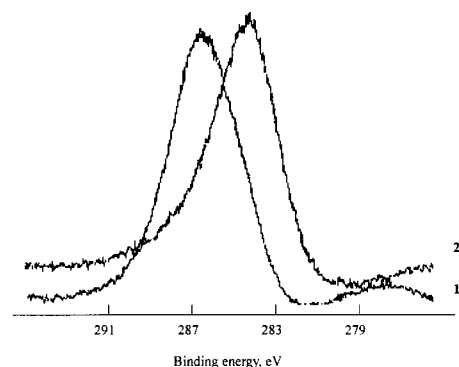


Fig. 4. C_{1s} spectra with sputtering time. 1) 0 min and 2) 15 min.

suggested that the deposited film of B_2O_3 be very thick in the worn scar surfaces.

The changes of Fe_{2p} binding energies with sputtering time are shown in figure 3. Binding energy of Fe_{2p} on the outer worn surface was about 710.9 eV with relative weak intensity in contrast with others. The broad peak should be contributed to different chemical states of iron species formed during the run. The binding energy at about 711 eV belonged to gamma $FeOOH$ or gamma or/and alpha Fe_2O_3 and the binding energy at around 708 eV might be caused by ferricyanides [9]. After the worn surface had been sputtered for 15 min, there appeared a strong signal located at the binding energies of 708.5 eV and 706 eV. These two peaks suggested that there should be two iron compounds in the inner worn surface, which were ferricyanides and base iron, respectively. After being sputtering for 35 minutes and 65 minutes, the photopeaks at the binding energy of 708.5 eV began to be gradually weakened with the increase of sputtering time. These phenomena indicated that the ferricyanides in the surface layer are very thick.

The binding energies of C_{1s} are shown in figure 4. The binding energy of 286.6 eV before being sputtered was caused by some species containing C-N bond. And the binding energy

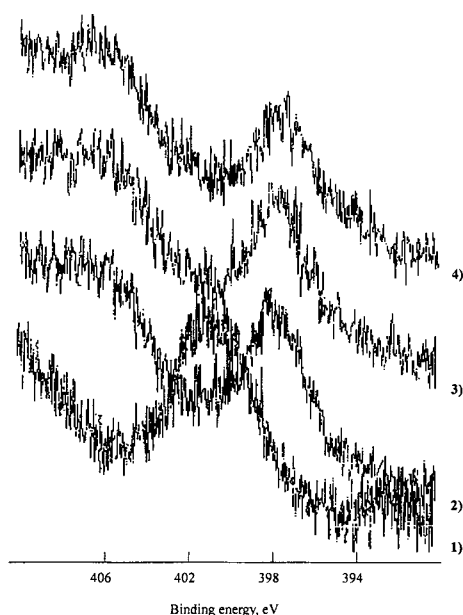


Fig. 5. Changes of N_{1s} binding energies with sputtering time. 1) 0 min, 2) 15 min, 3) 35 min, and 4) 65 min.

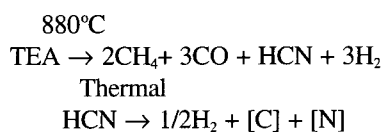
of 284 eV after being sputtered for 15min should be caused by ferricyanides, such as $[\text{Fe}(\text{CN})_6]^{3-}$. As such, there was similar information of chemical environments around the elemental carbon resulted from the XPS results of C_{1s} and Fe_{2p} .

Moreover, the binding energy of N_{1s} also confirmed that the existence of the ferricyanides in the worn surface. A wide peak of N_{1s} in figure 5 indicated that there were ammonium salt and/or cyanides at the binding energy of about 400 eV and cyanides at 398 eV. After being sputtered for 15 min and more, the peaks intensities at the binding energy of 402 eV became absent, and only one peak remained at around 398 eV.

Consequently, XPS analysis shows that the main components are iron oxides, ferricyanides and boron oxides on the worn scars.

Tribochemical mechanism

It is well known that carbon-nitrogen co-permeation technique of chemical heat treatment could improve wear resistance of material surface. TEA is a common compound as the resource of elemental C and N in the chemical heat treatment technique. Under the condition of high temperature, TEA will be decomposed into several species such as cyanides, and then the cyanides will be decomposed into atomic carbon and nitrogen with strongly activated states. These activated species permeate into metal substrate to form thin permeated layer. These reactions can be written as follows:

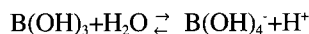


Many studies confirmed that chemical reaction would become easier under the rubbing condition than under the

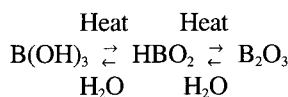
general condition. And even some impossible reactions under the general conditions can occur through rubbing [10]. Friction can cause to emit large amounts of exo-electrons, photons and particles with different charges [11], can produce nascent metal surfaces with strong catalysis [12], and can bring very high flash temperature at the asperities owing to plastic deformation and adhesion. These conditions apparently reduced reaction active energy and made some tribochemical reactions happening in a very short time. Therefore, it is possible on theory that the model compound can be decomposed and produce cyanides during rubbing. Actually, the results of XPS analysis have also proved this possibility.

Cyanides are apt to reacting with iron ion to create ferricyanides such as potash prussiate $[\text{Fe}(\text{III})(\text{CN})_6]^{3-}$ or yellow prussiate of potash $[\text{Fe}(\text{II})(\text{CN})_6]^{4-}$. Those are specific reactions for distinguishing iron ion from another ion in the system of inorganic chemical analysis. Elemental iron existed as the state of iron oxides owing to the nascent metal having strongly chemical reactivity. As such, there existed the above possibility for the ferricyanides to be produced in-situ during rubbing.

At the same time, at the existence of water, boric acid can be changed to $\text{B}(\text{OH})_4^-$ as follows:



But boric acid can also be decomposed under thermal conditions to form metaboric acid HBO_2 that has three kinds of structures under different thermal conditions. If the $\text{B}(\text{OH})_3$ is heated below 130°C , HBO_2 -III is formed. This has a layer structure in which B_2O_3 six rings are joined by hydrogen bonding between OH groups on the boron atoms. On the continued heating of HBO_2 -III at 130 - 150°C , HBO_2 -II is formed. This has more complex structure containing both BO_4 tetrahedra and B_2O_3 groups on chains linked by hydrogen bonds. Finally, on heating of HBO_2 -II above 150°C , cubic HBO_2 -I is formed in which all boron atoms are four-coordinate. The processes can be expressed as follows:

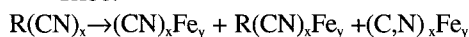


Therefore, boric acid exhibited good wear resistance due to its sandwich structure [8]. So the created boric acids by tribochemical reactions in-situ provided the wear resistance of the water solution containing borate of TEA. Because of being easily de-watered, under the action of high thermal, the boric acid produced a kind of de-watered product, boron oxide that is a glassy state under high temperature can give wear resistance.

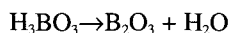
In tribochemistry with particular frictional reaction conditions, many reacted products are usually stoichiometric proportions. Based on the above analysis and the XPS results a tribochemical model can be suggested as below (borate of triethanolamine is shorten as BTEA):



Tribo.



Tribo.



Detailed research should be put to study on decomposition of BTEA and interactions between TEA and boric acid in water solution. Also water solution should be analyzed to probe any water soluble components from BTEA after rubbing.

Conclusions

- (1) Borate of triethanolamine exhibited good antiwear capability in water solution.
- (2) Surface film on worn scar was very thick and mainly consisted of H_3BO_3 , B_2O_3 and ferricyanides species.
- (3) The components of the surface film in the worn scar showed that tribochemical behavior resembles chemical heat treatment in this experimental.

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