Tribochemical interactions of boron carbides against steel

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Abstract

Auger electron spectroscopy and electron microscopy were used to investigate the surface chemistry and tribological properties of boron carbide sliding against steel. It was revealed that the interacting process was accompanied by the diffusion of the ceramic elements into steel and by the oxidation of the steel and ceramic surfaces due to the oxygen presence in the atmosphere. It was established that the oxidation process in air or during friction tests leads to a graphitized layer on the boron carbide surface under the B$_2$O$_3$ film. It was demonstrated that the oxidation caused a decrease in the friction coefficient of boron carbide sliding against steel.

1. Introduction

Boron-carbide-based ceramics exhibit a low density associated with high strength, hardness and wear resistance [1, 2]. They are being considered for engine components (tappet followers, rotary seals and rolling bearings) and other items operating in sliding contact with metal members [3]. With a variety of conditions, tribologically stressed elements cannot be lubricated by oils. Because of the heating of the contact surfaces and tribochemical effects, the interaction of ceramics with metal and environment occurs and, as is known, the friction coefficient and wear of the conjugated surfaces are substantially determined by the tribochemistry of the surfaces. The alterations in surface chemistry and tribological properties of the surface layers of boron carbide occurring by sliding ceramics against ceramics were previously studied [4–6]. The tribological properties of various ceramics sliding against steel have been described in ref. 7. However, the tribochemical behaviour of boron carbide sliding against steel is not yet extensively considered by the literature.

The purpose of the present work is to investigate the secondary structures formed on B$_4$C surfaces sliding in contact with steel.

2. Experimental details

The tests were performed on 5 mm × 5 mm × 15 mm samples using a Soviet M22-M and MT-68 pin-on-ring tribometers [8]. All friction experiments were conducted
with a load of 4 MPa at a sliding velocity of 1–15 m s⁻¹ for 1 h at room temperature in air without a lubricant. Hot-pressed boron carbide (Table 1) obtained in the Institute for Problems of Materials Science was used as the pin specimen (Fig. 1(a)), whose testing surface was finished by grinding to $R_a = 0.2 \, \mu m$ and had a profile of constant curvature. Steel containing 0.45 wt.% C (Rockwell C hardness, 42–45 HRC) was used for the ring specimen (Fig. 1(a)) whose testing surface was finished by grinding and polishing to $R_a = 0.05 \, \mu m$. To investigate the effect of composition changes of the boron carbide surfaces during oxidation on the tribological properties, samples pre-oxidized for 0.5 h in air in the temperature range 600–1200 °C were tested.

The surface of specimens tested at a sliding speed of 10 m s⁻¹ were investigated by metallography, X-ray diffraction (XRD) using Cu Kα-radiation, and Auger electron spectroscopy (AES) with a scanning Auger microprobe. The thickness of the layer analysed by AES was about 3 nm. In order to determine the diffusion depth of the elements inside the sliding surfaces, notched samples were fractured perpendicular to the sliding surfaces in the vacuum chamber of the Auger spectrometer, and then the virgin fractured surfaces were analysed (Fig. 1(b)). Quantitative analysis by AES was performed using relative sensitivity factors [9] and JAMP-10S software from JEOL Ltd. (Japan).

### Table 1

Selected properties of boron carbide used in this study

<table>
<thead>
<tr>
<th>Density (g cm⁻³)</th>
<th>Room temperature strength (MPA)</th>
<th>$H_V$ (GPa)</th>
<th>$K_{IC}$ (MPa m¹/²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Three-point bend</td>
<td>Four-point bend</td>
<td></td>
</tr>
<tr>
<td>2.51</td>
<td>450</td>
<td>360</td>
<td>30</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagrams of (a) the friction test configuration and (b) “three-dimensional” AES analysis.
3. Results and discussion

The friction coefficient of the investigated materials (Table 2) is normally in the range 0.4–0.8 at small sliding velocities (up to 6 m s⁻¹). For higher velocities (more than 10 m s⁻¹) it decreases in the range 0.12–0.16 (more details of the effect of test conditions on the tribological properties of B₄C sliding against steel have been given in refs. 10 and 11). Irrespective of the composition of the ceramics a dark-grey film was formed on the steel surface with a thickness dependent from the test conditions. AES analysis of the metal surface revealed iron, oxygen, carbon and boron on the wear track. While boron was observed at a depth of several micrometers, carbon and oxygen diffused down over more than 100 µm (Fig. 2). The Auger peaks (peaks 1–3 in Fig. 3(a)) related to carbon present on the surface and in the subsurface layer of the material correspond to carbide-type carbon. As is seen in Fig. 4, the sliding process induces the formation of a thin film on the steel surface; its composition as determined by the XRD technique showed Fe₃O₄ and Fe₂C compounds. This film cleaves under impact fracture of the sample in the Auger spectrometer chamber and cracks under penetration tests with a diamond indenter, showing brittle characteristics.

The analysis confirmed the presence of the same elements on both ceramic and steel surfaces [10]. Thus tribochemical reactions on the sliding surfaces result in the formation of a layer consisting of compounds in the Fe–C–O–B system. At the same time in some grooves of the wear track of the ceramics surface a cracking glassy film was observed (shown with an arrow in Fig. 5), having a morphology close to that of the similar film formed during the oxidation in air of B₄C (micrographs given in refs. 12 and 13). Solidified drops 2–5 µm in size were also observed (Fig. 5) the analysis of which demonstrated that the main components of those drops were boron, oxygen and iron. These drops can be classified as iron borates or iron-containing boria glass. The oxidation of iron and boron carbide during the friction experiments is then

<table>
<thead>
<tr>
<th>Sliding velocity (m s⁻¹)</th>
<th>1</th>
<th>3</th>
<th>6</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friction coefficient</td>
<td>0.6–0.8</td>
<td>0.45–0.5</td>
<td>0.45</td>
<td>0.12–0.16</td>
</tr>
</tbody>
</table>

TABLE 2
Friction coefficients of boron carbide against steel

![Fig. 2. Elemental depth profile of the steel surface.](image)
confirmed. The formation of those drops should be indicative of a liquid oxide layer present on the sample surface during wear tests. Taking into account that the melting temperature of $\text{B}_2\text{O}_3$ is about 450 °C, it seems reasonable assuming that the contact temperature was not less than 450–500 °C. When the ceramics slide on the steel surfaces at a high velocity, the flash temperature may be even higher and reach the melting point of the steel [7]. The oxidation of $\text{B}_4\text{C}$ in sliding contact with $\text{B}_4\text{C}$ was observed even earlier [6] but at higher temperatures. A liquid boron oxide film formed under these conditions should operate as a liquid lubricant. Since the surface temperature rises with the increase in sliding velocity, it is estimated that the oxidation at 15 m s$^{-1}$ was more pronounced and the lower friction coefficient was measured (Table 2).
The pre-oxidation of B₄C samples in air also leads to a decrease in the friction coefficient (Fig. 6). AES studies of the sample surfaces oxidized at 1200 °C demonstrated that under the B₂O₃ film a carbon layer was formed. This fact is confirmed by the elemental depth profiles (Fig. 7) showing the existence of a rather sharp boundary between carbon and B₄C. AES analysis (Fig. 3(b)) and XRD studies of the samples oxidized at 1200 °C showed the presence of graphite-type carbon on the surfaces. The graphite form is characterized by a step, where its position is labelled 4 in Fig. 3(b). This, from the obtained results, the assumption made in ref. 14 concerning the surface depletion of carbon during B₄C oxidation seems unacceptable. Graphite formed on the sample surface and having low energy shear planes, as well as B₂O₃, is probably responsible for the reduction in friction coefficient after oxidation at 1200 °C (Fig. 6) and microhardness of the surface layer observed in ref. 13. The fracture analysis of the boron carbide samples after the tests demonstrated that the tribochemical processes occurring in the surface layer resulted in the graphite formation and boron depletion, as it occurs during oxidation in air at much higher temperatures. The pattern of boron

Fig. 6. Friction coefficients as a function of B₄C oxidation temperature.

Fig. 7. Depth profiles of boron and carbon for the boron carbide sample after oxidation at 1200 °C.
and carbon distribution in the subsurface layer (a distinct boundary between stoichiometric B$_4$C and a carbon-enriched layer) is presented (Fig. 8(a)). The graphitization in the outermost surface layer (about 100 nm) was observed also for SiC single crystals sliding against iron [15] and polycrystalline sintered α-SiC [16].

The iron transfer on the surface layer of B$_4$C up to 10 µm depth corresponds to the thickness of a graphitized layer. In this layer under the surface a lower boron oxide B$_2$O can also exist [14]. However, the non-flatness of the sliding surfaces, a very small thickness of this layer and its location under the surface make it difficult to perform XRD studies satisfactorily and to confirm or deny B$_2$O formation.

During the test on the sample pre-oxidized in air for 0.5 h at 1200 °C, the change in boron and carbon concentrations involve a much larger depth (Fig. 8(b)). The zone of the minimum boron content appeared to be shifted down to 15–20 µm inside the sample. The presence of iron in the subsurface layer of ceramics was not observed in this case. Lower adhesion between ceramic and metal surfaces may also be one of the reasons for a lower friction coefficient after oxidation.

Proceeding from the data obtained during the measurements of temperature under the sliding surface, one can make the assumption of gradual wear of a graphitized layer. Thus for unoxidized B$_4$C the maximum median sample temperature (150 °C)

![Graph showing elemental depth profiles of B$_4$C samples](image_url)

Fig. 8. Elemental depth profiles of the B$_4$C samples tested (a) in the as-received condition and (b) after oxidation for 30 min at 1200 °C.
was achieved in 0.5 h after the commencement of sliding; for the oxidized sample it was achieved in 1.5 h. The experiments demonstrated also that, as a rule, the friction coefficient increased with longer sliding times. Further investigations showed that the increase in friction coefficient was associated with films of similar composition formed on the interacting surfaces. Covering of ceramic and steel surfaces with the transfer films leads to higher adhesion between the sliding surfaces. After a certain time (perhaps, after reaching some “critical” thickness) the brittle film on the metal surface fractures and cleaves which is associated with an abrupt decrease in the friction coefficient. Similar cycles are repeated continuously during experimentation.

Thus one can conclude that, on sliding of boron carbide against steel, two simultaneous processes occur, one leading to a decrease in the friction coefficient (B₄C oxidation associated with B₂O₃ and graphite formation) and the other resulting in its increase (transfer of ceramics on steel and vice versa).

4. Conclusions

(1) Sliding processes of boron carbide against carbon steel in air induce the following changes in the composition and structure of surface layers of metal and ceramic: (a) the saturation of the steel surface with carbon and its oxidation with oxygen from the air, leading to the formation of Fe₃C, Fe₃O₄ and, probably, iron boride Fe₃B; (b) the oxidation of the B₄C surface associated with the formation of B₂O₃; (c) the formation of a boron-depleted and carbon-enriched layer under the oxide film on ceramics, material with graphite-like carbon being revealed (the graphitization of the subsurface layer also occurred on the oxidation of B₄C in air above 1000 °C); (d) the diffusion of iron into boron carbide and boron into steel to a depth of not more than 10 μm under the experimental conditions.

(2) The oxidation of B₄C associated with graphite and liquid B₂O₃ formation caused a decrease in the friction coefficient of boron carbide sliding against steel.

(3) The transfer of ceramic components on the steel surface and iron transfer on the B₄C lead to an increase in the friction coefficient.

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References