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Friction and Wear Properties of Boron Carbide Coating under Various Relative Humidity

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Abstract: Friction and wear properties of the Boron carbide (B_4C) coating 100 nm thickness were studied under various relative humidity (RH). The boron carbide film was deposited on silicon substrate by DC magnetron sputtering method using B_4C target with a mixture of Ar and methane (CH_4) as precursor gas. Friction tests were performed using a reciprocation type friction tester at ambient environment. Steel balls of 3 mm in diameter were used as counter-specimen. The results indicated that relative humidity strongly affected the tribological properties of boron carbide coating. Friction coefficient decreased from 0.42 to 0.09 as the relative humidity increased from 5% to 85%. Confocal microscopy was used to observe worn surfaces of the coating and wear scars on steel balls after the tests. It showed that both the coating surface and the ball were significantly worn-out even though boron carbide is much harder than the steel. Moreover, at low humidity (5%) the boron carbide showed poor wear resistance which resulted in the complete removal of coating layer, whereas at the medium and high humidity conditions, it was not. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) analyses were performed to characterize the chemical composition of the worn surfaces. We suggest that tribochemical reactions occurred during sliding in moisture air to form boric acid on the worn surface of the coating. The boric acid and the tribochemcal layer that formed on steel ball resulted in low friction and wear of boron carbide coating.

Keywords: Friction, wear, boron carbide coating, relative humidity, X-ray photoelectron spectroscopy, auger electron spectroscopy

Introduction

Boron carbide (B_4C) hard coating has attracted attention to become a great candidate for tribological applications for protection from wear and corrosion due to their high hardness, high mechanical strength and other properties. It has been widely used in cutting tools, automobile components, and other potential applications such as protective films for hard disk [1-5].

Until now, only a few studies have been performed in order to investigate the tribological property and wear mechanism of B_4C coatings in sliding under effect of working environment. It has been reported that the coefficient of friction and wear of boron carbide varies significantly depending on the sliding conditions between two contacting surfaces [6-10]. In their study, Gogotsi *et al.* revealed that the friction coefficient was in the range of 0.4-0.8 at small sliding velocities (1-6 ms^{-1}), and was in the range of 0.12-0.16 at higher (more than 10 ms^{-1}), when boron carbide slid against steel [6]. The effect of relative humidity on friction and wear of B_4C-based materials was also studied by K. Umeda *et al.* [7]. The results showed that friction coefficient reduced with the increase in humidity. The tribological property of boron carbide thin film in nanoscale was also investigated using an atomic force microscope [8,9]. Even though the wear mechanism is very different between macro- and nanoscale, both sliding velocity and relative humidity showed their significant influence on friction and wear of the film. In previous work, the effect of CH_4 component in processing gas on mechanical and tribological properties of the sputtered boron carbide coating was examined [11]. In this study, we investigate friction behavior and wear property of coating under various relative humidity. The film was prepared by DC sputter deposition technique and is described below. We employed a reciprocating friction tester to investigate the friction behavior and wear of the coating at different relative humidity, in ambient environment. Steel balls were used as the counter specimen. Confocal microscope was used to observe worn surfaces and the scars on the balls after tests. Chemical structure and elemental composition of the original coating and worn surfaces were characterized using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

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Experimental details

Coating preparation

Before the coating process, a 20 nm thick Cr layer was deposited on a thermally oxidized Si (100) wafer to improve the adhesion of coating to the substrate. The boron carbide coating was then deposited by DC magnetron sputtering from a B_4C target without applying substrate bias. The system base pressure was 5×10^{-7} Torr, while the deposited pressure was 9 m Torr. A mixture of argon (Ar) and methane (CH_4) at 1.2 vol. % was used as processing gas for deposition. The substrate temperature and target power were 150°C and 400 W, respectively. The nominal thickness of the film was 100 nm, which was determined based on the deposited time with a constant deposition rate, calculated using a profilometer. Atomic force microscope (AFM) was use to observe the morphology of the film. Hardness and Young's modulus of the coated film were measured [11].

Friction test

A reciprocating friction tester was employed to investigate the tribological properties of the coating. Steel balls of 3 mm diameter were used as counter specimen. The tests were carried out without lubrication in ambient air, at room temperature. Prior to the tests, the ball specimens were cleaned to remove the surface contaminants. First, the ball was soaked with Hexane in 8 hours to remove the industry oil, and then subjected to ultrasonic cleaning in acetone and methanol solutions for 15 minutes each. Finally, the ball was dried under compressed nitrogen gas flow. All the tests were performed with the normal load of 0.3 N, which corresponds to a maximum Hertzian pressure of ~850 MPa. Sliding speed was 4.43 mm/s, and stroke length was 3 mm. The relative humidity was controlled and maintained at 5%, 45%, and 85% during the tests. To evaluate the wear of coating, friction tests were stopped after 2000, 5000 and 10,000 sliding cycles at all conditions of relative humidity. The tests were repeated at each condition at least five times to check the reproducibility of friction behavior.

Characterization of coating

After the tests, the worn surfaces of coating and the balls were observed using the NanoFocus μSurf confocal microscope. From the obtained images we selected the wear tracks and corresponding balls for further analyses. AES surface analysis was performed to examine the physical and elemental characteristics of the coating surfaces and wear scars of the balls. Accelerating voltage of emission and the current were 5 kV and 0.0113 μA, respectively. The working potential was 3 kV using Ar-ion whereas the current varied between 0.0080-0.0160 μA when doing depth sputtering. Under this working condition, the sputter rate was ~103 Å/min. when calibrated against SiO_2. For the ball specimens, sputter rate was ~ 34 Å/min. while the working potential and current was 2kV and 0.0106 μA, respectively. The chemical composition and homogeneity of original coating and worn surfaces were studied by X-ray photoelectron spectroscopy (XPS). XPS spectra were acquired using a monochromated Al Ka source (1486.6 eV) in a working vacuum at 1×10^{-9} Torr. Working potential and current of ion gun was 15 kV and 24 mA, respectively. The sputtering rate was ~45 Å when calibrated against SiO_2. Binding energies were corrected by indexing the C1s peak to its characteristic level of 284.6 eV.

Results and discussion

Friction behavior

Figure 1 shows the representative curves of friction coefficient at humidity of 5%, 45% and 85%. It is clear that humidity strongly affected the friction behavior of boron carbide coating. Friction coefficient decreases with the increase of relative humidity. As shown in this figure, the friction coefficient in dry air was high and unstable from the beginning of the test, whereas it was much lower and more stable for the tests carried out in humid air. At RH of 5%, the coefficient of friction was 0.42, and it considerably decreased to 0.11 and to 0.09 with the tests at RH of 45% and 85 %, respectively. At least three tests at each humid condition showed the similar friction behavior. The friction coefficients were calculated with the deviation less then 15% of their mean value in steady state.

Previously, K. Umeda *et al.* and P. Larsson *et al.* have earlier studied the effects of relative humidity on the friction of boron carbide in sliding contact [7,10]. They reported that the friction coefficient decreased with the increase in relative humidity, from 0.8-0.95 at dry air (RH<10%) to 0.2-0.3 when relative humidity was above 70%. This result was achieved by measuring the friction of boron carbide surfaces slid against themselves. However, it showed the similar tendency of friction behavior to the experiments we have done. The friction property of boron carbide coating in nanoscale was investigated using an atomic force microscopy tip slid over the film by R. Prioli *et al.* [9]. It was reported that the friction increased with the increase in humidity and the reason was due to the interaction between boron atoms and air moisture. At high humidity, boron carbide surface was partially oxidized resulted in high friction at the tip-surface interface [9]. However, the increase of adhesion force between the AFM tip and coating surface in high humid environment is a reason leading to high friction. In our case, we suggest the tribochemical reactions happened at contacting surfaces of the boron carbide film and steel ball during sliding under humid condition of environment resulted in the low friction of boron carbide film.

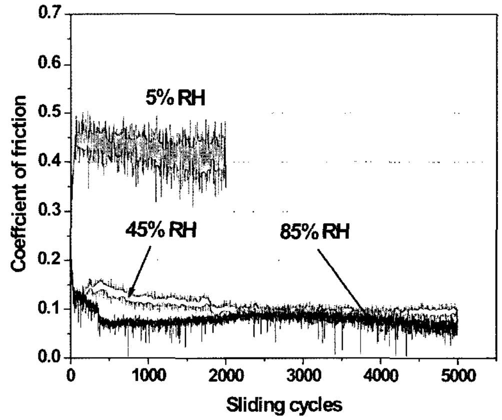
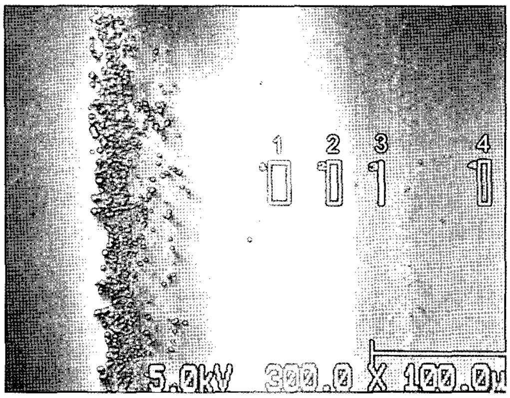
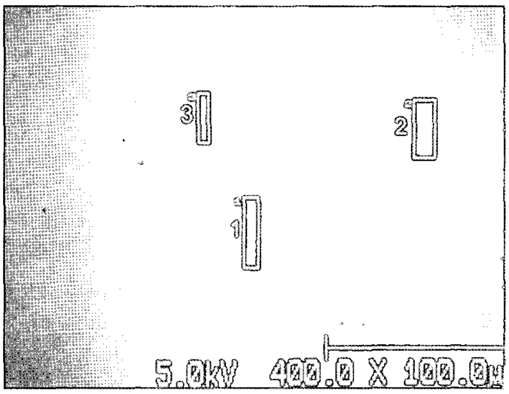


Fig. 1. Typical friction coefficients of B_4C coating slid against steel ball under various relative humidity.



(a)

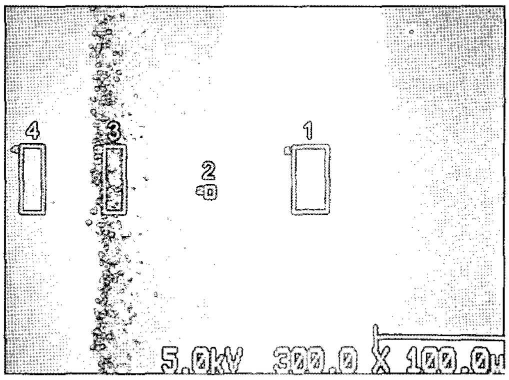


(b)

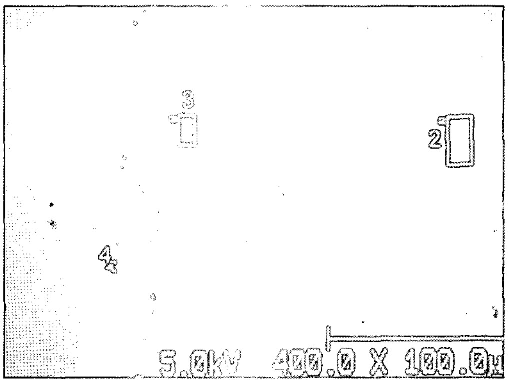
Fig. 2. SEM images of worn surface of B_4C coating after testing 2000 sliding cycles. The relative humidity was 5% (a) and 45% (b). The boxes are selected regions for AES analysis.

Wear property

Figure 2 shows scanning electron microscope (SEM) images of B_4C film worn surfaces after 2000 sliding cycles. Figure 2(a) is a typical worn surface of the coating tested at 5% of RH. Wear track is well defined with the accumulation of wear particles on both the sides of the worn area. The image also shows the distinct boundaries of the areas inside the wear track. It could be seen that the coating layer was removed partially under sliding contact with the ball specimen. According to the AES results, boron, carbon, and oxygen elements are present in area #4 (out of the wear track). With respect to XPS result [11] it could be confirmed that was the original coating. The elemental composition of areas #2 and #3 (darker regions inside wear track) was similar to the original coating implied that the B_4C still survived. By contrast, no boron detected in area #1 (center of the wear track), which confirmed the complete removal of the film. Moreover, the strong presence of chromium in this area indicated that the chromium layer deposited underneath B_4C coating was exposed entirely. In comparison, the worn surface of the test made at RH of 45 % shown in Fig. 2(b) shows very slight damage of the film, with the same number of sliding cycles. AES results for area #1 and #3 of wear track showed the similar composition to the original (area #2). Therefore, together with the high and unstable friction coefficient shown above, we conclude that the B_4C possesses high friction and poor wear resistance in dry air.



(a)



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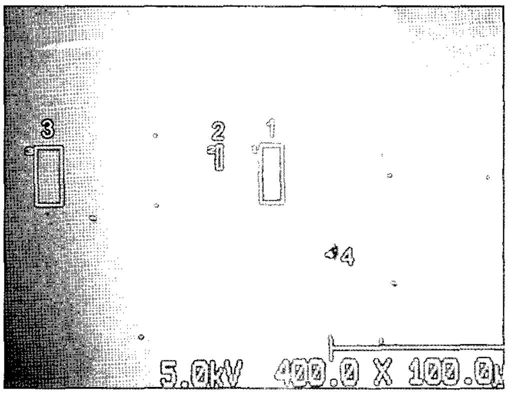

(c)

Fig. 3. SEM images of worn surfaces of B_4C film after testing 5000 sliding cycles. The relative humidity was 5% (a), 45% (b) and 85% RH (c), respectively.

The SEM images of worn surfaces after 5000 sliding cycles, under various relative humidity are showed in Fig. 3. The boxes denoted the AES analyzed areas. The test at 5% of RH resulted in the severe wear of the film as can be seen in Fig. 3(a). Elementary analytical result for a typical region (region #1, Fig. 3(a)) inside the wear track indicated that the B_4C film was removed completely without any trace of boron shown (see Fig. 4). Figures 3(b) and 3(c) are the images of wear track of tests conducted at 45% and 85% RH, respectively. The film shows less damage in humid environment than in dry air, even

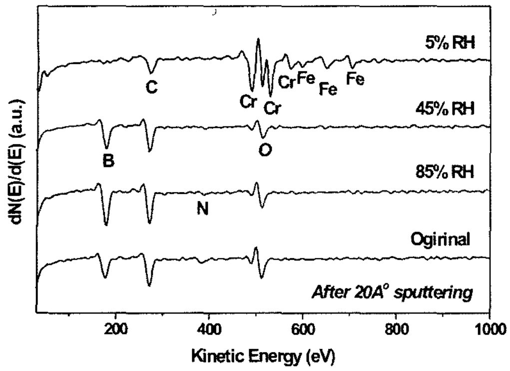

Fig. 4. AES analysis results for the typical worn surfaces tested at various relative humidity.

though wear tracks are well defined. One can note that, the wear particles came out from the wear tracks in the tests at dry air (Fig. 2(a) and 3(a)) reduced significantly in the test at 45% RH. They almost disappeared at 85% RH. Examination by AES for area #1 of worn surfaces at 45% and 85% of RH showed no evidence of complete failure of coating. Elemental composition of these regions is similar to that of original surface with the presence of boron, carbon, oxygen and a small amount of nitrogen (see Fig. 4).

The AES scanning results for typical region of the wear tracks made by the tests at RH of 5%, 45% and 85% are displayed in Fig. 4. Data were acquired after 20Å sputtering to remove the surface contaminants. As can be seen, the elemental composition of the worn surfaces tested at humid environment possesses similar components to that of original coating, whereas at 5% RH chromium appeared severely in whole of wear track. This means the B_4C film was worn out rapidly in the case of test in dry air. Moreover, auxiliary tests by extending the number of sliding cycle to 10,000 also exhibited the severe wear of B_4C layer at the RH of 45% while the coating was considerably remained in case of at 85% RH after the same cycles.

The influence of humidity on the wear of B_4C coating is displayed in Fig. 5. The nominal thickness of original coating is shown by the dotted line. The thickness of coating after 2000, 5000 and 10,000 sliding cycles was measured and calculated in comparison with the original coating. As mentioned above, B_4C film exhibited the poor wear resistance at dry air by showing the complete wear of B_4C layer, even after 2000 sliding cycles. Thus the wear evaluation of coating for the tests at 5% RH was excluded. It shows obviously that the wear resistance of boron carbide is increased significantly with the increase of relative humidity. The film still remained even after 10,000 sliding cycles at high humidity (85% RH), whereas it was completely worn out by the test at RH of 45%, with the same number of sliding cycle.

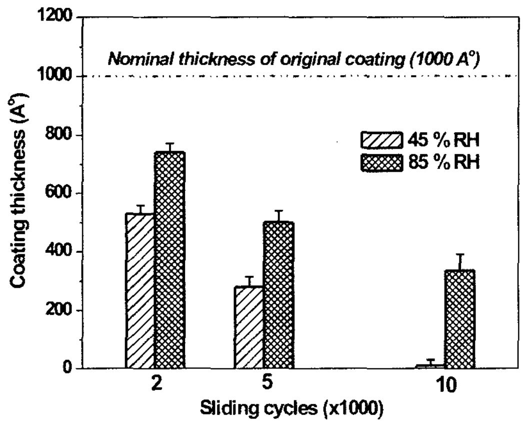

Fig. 5. The effect of relative humidity on wear property of boron carbide coating. Sliding cycles was 2000, 5000 and 10,000 respectively.

The representative wear track of B_4C coating was examined by XPS analysis. Figure 6(a) is the B1s spectrum for worn surface of the test at 45% RH while C1s and O1s spectra are shown in Fig. 6(b) and 6(c). The full widths at half maximum (FWHM) of B1s, C1s and O1s spectra are large indicated that the boron, carbon and oxygen atoms in the worn area are in

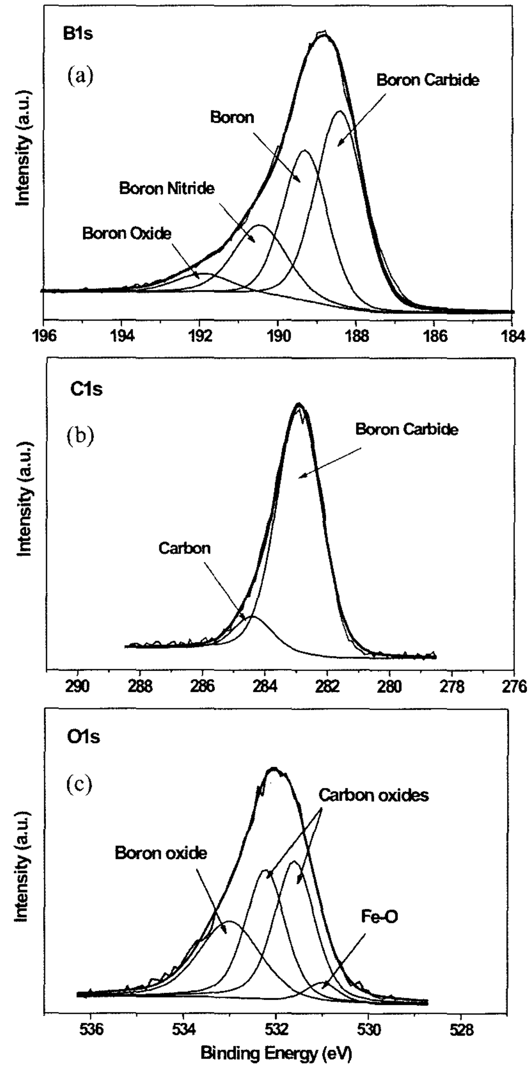

Fig. 6. B1s (a), C1s (b), and O1s (c) X-ray photoelectron spectra for worn surface of B_4C coating. The relative humidity was 45%.

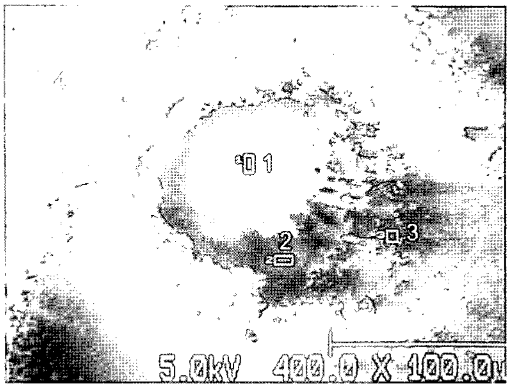

Fig. 7. SEM image of worn surface of ball specimen after testing test at 5% of RH and 2000 sliding cycles.

different chemical bonding states. The B1s signal is composed of four components with the binding energies centered at 188.4, 189.3, 190.5 and 192 eV, which plausibly corresponds to boron carbide (major peak), elemental boron, boron nitride and boron oxide (B_2O_3) respectively [13,14]. However, it was reported that the peak at 189.3 eV was close to the binding energy of BC_3 [15]. The C1s spectrum obtained from the wear track displays two discrete signals that are attributed to boron carbide (at ~283 eV) and graphitic carbon (at ~284.5 eV) [13-15]. For the original coating, B1s and C1s spectra gave similar results except that a smaller amount of the boron oxide was detected [11]. That means the boron carbide surface was experienced an oxidation process. Regarding the O1s spectrum (Fig. 6(c)), the peak at ~533 eV is assigned to boron oxide, whereas the peaks at ~531.6 and 532.3 eV are close to the carbon oxides [14]. The small signal at ~531 eV is attributed to Fe-O bond [14] due to the oxidation of the ball surface. Hence, the XPS analysis results confirmed that there was a tribochemical oxidation of the steel ball and boron carbide coating during the sliding process. Similar results were also reported by Gogotsi *et al.* [6].

Figure 7 is wear scar of the ball made by the test at 5% RH and 2000 sliding cycles. The B_4C film and counter-body steel ball have undergone the severe wear in dry contact. As can be seen, the ball specimen is abraded and is severely worn out. Following the AES results, iron is dominated in area #1, while in area #2 the elemental composition is similar to that of boron carbide film. This confirms the transfer of ceramic component to the ball at area #2. Regarding the worn surface of the coating (Fig. 3(a)), boron, carbon, oxygen and iron have been detected in the wear debris. Thus, the tribochemcial oxidation and the material transfer of coating to the ball specimen simultaneously occurred during sliding leading to the high friction and wear of the film in this case. In literature, it is reported that the wear of boron carbide coating in humid air was due to the tribochemical reactions that occurred at contact area [6,10,12]. The low friction and wear of boron carbide coating in humid environment was achieved by experimental results shown above. The carbon in graphitic phase in the structure of the coating following the XPS results (Fig. 6(b)) might be a reason. AES analytical result for the ball tested at 85% of RH (not shown here) shows a tribochemical layer covered the worn area. In contrast, this layer could not be seen in the balls tested at dry air. Therefore, the tribochemical layer might play an important role in reducing of friction and wear of the boron carbide coating. Moreover, Erdemir *et al.* and Dvorak *et al.* have reported that the boron oxide on boron carbide surface reacted with the moisture in air at room temperature to form boric acid as: $B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$ [16-18]. Therefore, it is suggested that the forming of boric acid on top layer of B_4C coating also contributed to the low and stable friction of boron carbide coating in high humidity.

Conclusions

In this work, the effects of relative humidity on friction and wear properties of boron carbide coating in sliding contact with steel balls were studied. The results are summarized as follows.

1. Tribological properties of boron carbide coating were strongly affected by relative humidity of environment. The friction coefficient was reduced and the wear resistance of the film was increased with the increase in relative humidity.
2. The wear mechanism of boron carbide was mainly tribochemical process and the material transfer to the counter-body.
3. The low friction of the B_4C coating at high relative humidity might result from the forming of tribochemical layer on the contact area of the ball and the form of boric acid on worn surface of the film.

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