Effect of Negative Bias Voltage on Tribological Properties under High Relative Humidity Environment and Corrosion Resistance of Boron Carbide Coatings

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Abstract: Humid air is a very important service environment, in which metal friction parts should be enhanced to offer excellent corrosion resistance and wear resistance. The B4C coating is an excellent candidate material to enhance the corrosion resistance and tribological behaviors. The purpose is to investigate the effect of negative bias voltages on the tribological properties of B4C coatings under a high relative humidity environment. Amorphous B4C coatings were successfully prepared by closed field unbalanced magnetron sputtering technology and its microstructure, hardness, elastic modulus, adhesive force and tribological properties were systematically studied. Results demonstrate that the B4C coatings deposited at each negative bias voltage have a columnar structure and the surface roughness remained unchanged (about 1.0 nm), while the thickness, hardness, elastic modulus and adhesion force increase first and then decrease with the negative bias voltage increasing. Among them, the B4C (−50 V) coating showed the best mechanical properties. It should be noted that the B4C (−50 V) coating with an excellent corrosion resistance also exhibits the lowest friction coefficient (~0.15) and wear resistance (7.2 × 10−7 mm3 N−1 m−1) under humid air (85% RH). This is mainly due to the tribochemical reaction of B4C during a sliding process to produce boric acid at the sliding interface. B4C coatings can provide an excellent corrosion resistance and high wear resistance due to their high chemical stability and high hardness.

Keywords: negative voltage bias; high relative humidity; boron carbide coating; tribological performance; corrosion resistance

1. Introduction

Metal friction pairs face various atmosphere environments during service, such as high temperature, methane, dry nitrogen, dry air and humid air [1–4]. In particular, humid air is a very important service environment, and the surface of metal friction parts should be modified to have a high hardness and high chemical inertness in order to offer an excellent corrosion resistance and wear resistance. The ultra-high hardness of boron carbide (B4C) ceramics is second only to the hardness of diamond and cubic boron nitride in nature [5–7]. At the same time, it also possesses excellent chemical stability [8,9]. Therefore, the B4C coating is an excellent candidate material under high humidity conditions to enhance the corrosion resistance and tribological performances [10].

The development of magnetron sputtering sources over recent years has attracted extensive attention to the B4C coating deposited by closed field unbalanced magnetron sputtering technology [11–14]. The magnetron sputtering technology can produce high kinetic energy and density plasma, which has the advantages of a faster deposition rate, larger deposition area, lower deposition voltage and lower deposition temperature and easy industrial production. In addition, the prepared B4C coatings by closed field unbalanced magnetron sputtering technology have excellent physical and chemical properties, such
as excellent mechanical properties, a high adhesion, uniform and compact surface and small roughness [7]. If a suitable negative bias is applied during the deposition process, the sample can be cleaned and activated in the deposition chamber, which is conducive to improving the coating bonding strength, increasing the coating nucleation density in the nucleation stage and the coating density in the growth process, increasing the surface heat energy and introducing lattice defects in the surface area of the interlayer, so as to promote diffusion and reaction and improve the bonding force [15]. Based on the above advantages, closed field unbalanced magnetron sputtering deposition technology has been widely concerned and applied.

The appropriate negative bias voltage can effectively increase the energy and flow of sputtered ions, and then improve the mechanical properties such as hardness and adhesive force, as well as the tribological properties. Therefore, B₄C coatings were prepared by unbalanced closed field magnetron sputtering equipment, and the effects of negative bias voltage on the cross-section and surface morphology, thickness, microstructure and bonding strength of B₄C coatings were systematically investigated. At the same time, the tribological properties of B₄C coatings in humid air were investigated. The results of this paper have an important guiding significance for the deposition of B₄C coatings with excellent mechanical properties, low friction and high wear resistance by closed field unbalanced magnetron sputtering technology.

2. Materials and Methods

An unbalanced closed field magnetron sputtering device—UPD 650 (Teer, Droitwich, UK) was used to sputter one B₄C target and two Cr targets in argon (Ar) atmosphere and polish (Ra ≤ 0.03 µm). Amorphous B₄C coatings were successfully fabricated on 304 L stainless steel. Before deposition, the samples were ultrasonically cleaned with acetone and ethanol for 30 min to remove pollutants, and then dried with dry nitrogen. After being introduced into the deposition chamber, the samples were firstly etched by Ar⁺ under a bias voltage of −500 V for 30 min to further remove the residual organic matter and other impurities on the surface. Subsequently, a chromium (Cr) intermediate layer of ~200 nm was deposited by sputtering a high-purity Cr target in Ar atmosphere for 10 min to improve the bonding force. Finally, B₄C coatings with different properties were successfully deposited on the substrate by adjusting the negative bias voltage (0 V, −50 V, −100 V, −150 V). The specific deposition conditions were reported in our previous publications [16].

The cross-section and surface morphology of B₄C coatings were observed by SEM—JSM-6701F (JEOL, Tokyo, Japan). The surface morphology of the coatings was observed by atomic force microscopy—AFM (CSPM4000, Ben Yuan Nanometer Instrument Co., Ltd., Beijing, China), with a scanning area of 10 µm × 10 µm. The crystal structures of B₄C coatings and B₄C target were studied by the X-ray diffractometer—XRD (D/Max-2400X, Rigaku, Tokyo, Japan) with Cu Kα X-ray of monochromatic source. The Raman spectra of the coating in the range of 100–1800 cm⁻¹ were studied by the Lab-RAM HR Evolution Raman spectrometer. A nano indentation device (TTX-NHT2, Anton Paar, Graz, Austria), equipped with a diamond indenter tip, was used to measure hardness and Young’s modulus of the deposited coatings, and the indentation depth did not exceed 10% of the coating thickness to minimize the effect of substrate. The adhesions of B₄C coatings were measured with a CSM scratch instrument equipped with a diamond tip.

The tribological properties of deposited B₄C coatings in humid air (85% RH) were evaluated by CSM tester in pin-on-disk reciprocating mode. The friction and wear experiments were carried out at room temperature. The GCr15 ball with a radius of 3 mm was used as mating ball, normal load was 2 N, amplitude was 5 mm, sliding frequency was 5 Hz, and each sliding revolution was set to 10,000 cycles. In order to reduce the experimental error and obtain reliable experimental results, the friction test under each test condition was repeated at least three times. After the friction test, 3~5 positions were randomly selected on the wear tracks by two-dimensional optical profiler to measure wear loss; then, wear rates were obtained according to the formula:
Wear rate = Wear loss/(Applied load × rubbing distance). Moreover, the sliding interfaces after friction tests were analyzed by Optical microscope and Scanning electron microscope. An electrochemical workstation (PGSTAT302, Metrohm Autolab, Utrecht, The Netherlands) was used to perform the potentiodynamic polarization tests to measure the corrosion resistance of 304 L steel sheet and B₄C coating. A standard three electrode system was used and immersed in 3.5 wt.% NaCl solution for 30 min to obtain a stable open circuit potential (OCP). The action potential polarization experiments were carried out at a scanning rate of 2 mV/s at room temperature, and the applied potential was increased from −0.5 V below the stable OCP.

3. Results

3.1. Properties of the Boron Carbide Coatings

Figure 1 shows the SEM section morphology and AFM surface morphology of B₄C coatings. It was observed that the coating was composed of a Cr bonding layer and B₄C layer, in which the thickness of the Cr bonding layer was about 0.22 μm. The thickness of the B₄C layer was 1.40 μm, 1.46 μm, 1.59 μm and 1.52 μm, respectively, when the negative bias voltage was 0 V, −50 V, −100 V and −150 V. The reason why the coating thickness decreased slightly when the negative bias voltage was −150 V may be that the energy of the deposited atomic clusters was too large due to the high bias voltage. As shown in the illustration in Figure 1, the surface of the B₄C coating under different negative bias voltages was smooth, flat and dense, and the surface roughness was 1.2 nm (0 V), 0.9 nm (−50 V), 1.0 nm (−100 V) and 1.10 nm (−150 V), respectively, showing a trend of first decreasing and then increasing. In addition, it was observed that, except for depositing the B₄C coating with a bias voltage of 0 V, B₄C under other bias voltages showed an obvious columnar structure, and the higher the negative bias voltage, the more obvious the columnar structure was. Combined with the analysis of the surface roughness, the application of an appropriate negative bias voltage (−50 V) could make the microstructure of the film more compact and the surface roughness decrease. However, with the further increase in the bias to −150 V, the columnar structure became coarser and the roughness increased slightly, indicating that the high bombardment energy of Ar⁺ ions would increase the surface roughness of the film.

![Figure 1](image1.png)

**Figure 1.** SEM section morphology (a) and AFM surface morphology (b) of B₄C coating under different negative bias voltages.

The Raman spectrum of the B₄C coating is shown in Figure 2a. Obvious characteristic peaks of amorphous carbon were not observed, namely the D peak and G peak, which indicated that the B₄C coating did not contain free carbon. Therefore, according to the boron carbide phase diagram [17], we suggest that the deposited coating was mainly composed
of B₄C. By comparing the Raman spectrum and XRD spectrum of the B₄C coating and B₄C target (Figure 2b), it was concluded that the deposited B₄C coating was amorphous.

![Raman and XRD spectra](image)

**Figure 2.** Raman (a) and XRD (b) analysis of B₄C coating and B₄C target.

### 3.2. Mechanical Properties of B₄C Coatings

As shown in Figure 3a, the microhardness and elastic modulus of the B₄C coating increased first and then decreased with the increase in a negative bias voltage. In particular, when the negative bias voltage was −50 V, the microhardness and elastic modulus of the B₄C coating were the largest, about 32.4 GPa and 280 GPa, respectively. Figure 3b shows the bonding strength of B₄C coatings under different negative bias voltages, measured by a CSM scratch tester and showing the results. With the increase in a negative bias voltage, the bonding strength of the B₄C coatings first increased and then decreased, and reached the maximum at −50 V, which was 15.5 N (0 V), 20.5 N (−50 V), 20.2 N (−100 V) and 17.2 N (−150 V), respectively. Applying an appropriate negative bias voltage can effectively increase the energy and density of deposited clusters, which would lead to a strong bombardment, resulting in a more dense structure, higher microhardness and bonding force. However, if the negative bias voltage were to rise to −150 V, the energy and density of the deposited clusters could be too large. On the one hand, too large, deposited clusters would destroy the dense structure of the coating; on the other hand, too energetically deposited clusters would sputter out the atoms in the coating and cause back splashing, which would also destroy the dense structure of the coating; thus, weakening the mechanical properties of the B₄C coating.

![Mechanical properties graph](image)

**Figure 3.** Mechanical properties (a) and adhesive force (b) of B₄C coatings deposited at different negative bias voltages.

### 3.3. Tribological Performances and Corrosion Resistance of B₄C Coatings

Figure 4a shows the friction curves of B₄C coatings prepared by different negative bias voltages under a high relative humidity (85% RH). It was observed from Figure 4a that each B₄C coating had a low friction coefficient and a common feature: these friction curves started from a high value, then, gradually, decreased to a steady-state value accompanied
by large fluctuations. It was found from Figure 4b that both the friction coefficient and wear rate first decreased and then increased with the increase in a negative bias voltage. When the negative bias voltage was 0 V, −50 V, −100 V and −150 V, the friction coefficient of the B₄C layer was 0.21, 0.15, 0.28 and 0.28, respectively; the specific wear rates were 9.65, 7.24, 7.57 and 10.49 × 10⁻⁷ mm³·N⁻¹·m⁻¹, respectively.

![Figure 4](image_url)

**Figure 4.** Friction curves (a) and wear rates (b) of B₄C coatings preformed under humid air (85% RH).

Figure 5 shows the optical morphology of disc wear tracks of the B₄C coating under different negative bias voltages under humid air. It was observed that the wear tracks of the B₄C coating were relatively similar—there were many wear particles around the wear tracks, the interior of the wear tracks was very smooth with small cracks and obvious furrows were also observed. This indicated that fatigue wear and abrasive wear occurred in the friction process. Figure 6 shows the wear scar morphology of the GCr15 steel balls under different negative bias voltages. It was seen that the morphology of each wear scar was also relatively similar—the wear scars were a regular circular, many wear particles were scattered around and there were deep furrows inside.

![Figure 5](image_url)

**Figure 5.** Optical microscope images of wear tracks for B₄C coating deposited at different negative bias voltages—0 V (a), −50 V (b), −100 V (c) and −150 V (d), tested at 85% RH.
In order to further analyze the reasons for the best tribological properties of the B$_4$C (−50 V) coating, the wear track surface of the B$_4$C (−50 V) coating was investigated by SEM and EDS. As shown in Figure 7, there were some abrasive particles at the edge of the wear track of the B$_4$C (−50 V) coating and small furrows inside the wear track, which indicated that abrasive wear occurred during the friction process. In the corresponding EDS diagram, it was observed that the O element obviously accumulated on the wear debris at the edge of the wear track, which indicated that the B$_4$C coating was oxidized during friction and then reacted with water vapor to generate boron oxide (B$_2$O$_3$) or boric acid (H$_3$BO$_3$) [16]. This was why the B$_4$C coating obtained low friction in a high humidity atmosphere.

![Figure 6](image_url)

**Figure 6.** Optical microscope images of GCr15 worn scars for B$_4$C coating deposited at different negative bias voltages—0 V (a), −50 V (b), −100 V (c) and −150 V (d), tested at 85% RH.

![Figure 7](image_url)

**Figure 7.** SEM images (a) and elemental EDS maps (b) of the disc worn surfaces for B$_4$C coating (−50 V) performed under 85% RH condition.
In conclusion, the B$_4$C (−50 V) coating showed the best tribological properties at a high relative humidity (85% RH), and its friction coefficient was about 0.15 and the wear rate was about $7.24 \times 10^{-7}$ mm$^3$·N$^{-1}$·m$^{-1}$. Hardness was the main factor to evaluate wear resistance by the classical wear theory [18]: the harder the material, the more wear-resistant it is. In addition, the high elastic modulus, adhesion and denser microstructure can play a better bearing role. Therefore, the B$_4$C (−50 V) coating with the highest hardness, elastic modulus, adhesion and a denser columnar structure, had excellent friction and wear performances.

Considering that metal friction parts were prone to serious corrosion in a high humidity environment, we further compared and evaluated the corrosion resistance of a 304 L steel sheet and B$_4$C (−50 V) coating with an electrochemical workstation (PGSTAT302, AutoLab). It is well known that the resistance of corrosion can be estimated according to the corrosion current density ($I_{corr}$) and corrosion potential ($E_{corr}$) [19–21]. It was observed from Figure 8 that the $I_{corr}$ value of the B$_4$C coating was about $7.0 \times 10^{-8}$ A·cm$^{-2}$, and the $I_{corr}$ value of the 304 L steel sheet was about $3.0 \times 10^{-6}$ A·cm$^{-2}$. Moreover, the $E_{corr}$ value of the B$_4$C (−50 V) coating positively increased from −0.51 V of the 304 L sheet to −0.31 V of the B$_4$C (−50 V) coating. In short, the B$_4$C (−50 V) coating showed a lower corrosion current and higher corrosion potential than the 304 L steel substrate; that is, the B$_4$C coating significantly improved the corrosion resistance of the 304 L steel substrate. In addition, as shown in Figure 8b,c, the surface of the B$_4$C (−50 V) coating after the corrosion attack before the test had no obvious change compared with that before the corrosion attack. It was seen that the B$_4$C (−50 V) coating on the inner wall of the 6063 Al pipe could maintain stability in the corrosive medium, effectively prevent the penetration of corrosive medium and play a good protective role for the 6063 Al pipe.

![Figure 8](image_url)

**Figure 8.** The polarization curves (a) of B$_4$C coating deposited at −50 V and 304 L steel substrate in 3.5 wt.% NaCl solution, SEM image of B$_4$C coating before (b) and after (c) corrosion attack.
4. Conclusions

In view of the serious corrosion and wear of metal friction parts under high relative humidity conditions, B₄C coatings with excellent friction and wear properties were successfully prepared on 304 L steel sheets by closed field unbalanced magnetron sputtering equipment, and the effect of a negative bias voltage on mechanical properties and tribological properties under a high relative humidity environment were investigated. The main conclusions were as follows:

- The surface of the amorphous B₄C coatings under different negative bias voltages was smooth, dense and columnar. With the increase in a negative bias voltage, the thickness, microhardness, elastic modulus and bonding force of the coatings first increased and then decreased. Overall, the mechanical properties of the B₄C coating were the best when the negative bias voltage was −50 V.

- B₄C coatings showed excellent tribological properties in humid air with 85% RH, and the tribological performances increased first and then decreased with the increase in a negative bias voltage. When the negative bias voltage was −50 V, the B₄C coating showed the best friction reduction and wear resistance in humid air with 85% RH; the friction coefficient of the B₄C coating was as low as 0.15 and the wear rate was 7.2 × 10⁻⁷ mm³·N⁻¹·m⁻¹.

- The corrosion current density (Icorr) of 304 L steel substrate was about three orders of magnitude higher than the B₄C (−50 V) coating. The corrosion potential (Ecorr) value positively increased compared with that of the 304 L steel substrate. Therefore, the B₄C coating remarkably enhanced the resistance to corrosion of the 304 L steel substrate.

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