Microstructure and tribological properties of ternary BCN thin films with different carbon contents

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A B S T R A C T

Boron carbon nitrogen (BCN) thin films with different carbon contents are deposited on high-speed steel substrates by reactive magnetron sputtering (RMS) and their microstructure and tribological properties are studied. The BCN films with carbon contents from 26.9 wt.% to 61.3 wt.% have an amorphous structure with variable amounts of carbon bonds (sp²C–C, sp²C–N and sp³C–N bonds). A higher carbon content enhances the film hardness but reduces the friction coefficient against GCr15 steel balls in air. BCN films with higher hardness, lower friction coefficient, and better wear resistance can be obtained by increasing the carbon content.

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1. Introduction

Transition metallic nitride hard coatings such as TiN (2–3 μm thick) are used as surface wear resistant materials on cutting tools and dies because of the high hardness (21 GPa to 26 GPa)[1,2]. However, the high friction coefficient (about 0.7) of TiN limits wider applications in this area[3] because the desirable wear resistance must be in conjunction with both high hardness and low friction coefficient[4]. Therefore, hard films with low friction coefficient are crucial to applications to cutting tools and dies, especially high-speed cutting tools.

Carbon nitrogen (CNx) films have been extensively studied because of the high hardness (6 GPa to 18 GPa) and lower friction coefficient (0.2 to 0.3)[5,6]. However, the poor thermal stability at elevated temperature and poor adhesion to the substrate has hampered their use in the cutting tool industry[7,8]. In comparison, ternary boron carbon nitrogen (BCN) films possess better mechanical properties and thermal stability[9,10] and may be more suitable. Presently, several deposition techniques such as chemical vapor deposition (CVD)[11], plasma-enhanced CVD[12,13], ion beam enhanced deposition (IBED)[14], and reactive magnetron sputtering (RMS)[15] are used to synthesize ternary BCN thin films. Among these techniques, RMS has the advantages with respect to optimization of film composition by simply changing the target power. Moreover, it has been reported that BCN films generally have an amorphous structure consisting of hybridized chemical bonds of B–N, B–C, C–C and C–N, which results in hardness values ranging from 8 GPa to 35 GPa[10]. However, the tribological behavior is not as good as expected. For example, Zhou, et al. have shown that the friction coefficient of BCN films with 49 at% B, 42 at% C, and 9 at% N is 0.8 as measured by a pin-on-disk tribometer during sliding against the SUS440C ball in air[16]. Therefore, the friction coefficient of these BCN films against steel in air is still high and more work must be done to decrease the friction coefficient. In this respect, changing the carbon...
contents in BCN may yield the desirable results while retaining the high hardness.

In the work reported in this paper, BCN thin films are deposited by reactive magnetron sputtering. The carbon contents in the BCN films are adjusted by changing the graphite target power. The microstructure and tribological properties of the BCN films with different carbon contents are studied systematically in order to find the best composition that yields both high hardness and low friction coefficient. The tribological behavior is discussed from the perspective of chemical bonding and film microstructure.

2. Experimental details

The BCN films were deposited on high-speed steel (W18Cr4V) substrates by a reactive magnetron sputtering system schematically depicted in Fig. 1. High purity argon (99.999%) was used as the sputtering gas and high purity nitrogen (99.999%) was used as the reactive gas. The sintered graphite targets (435 mm × 94 mm × 8 mm) and sintered B₄C targets (435 mm × 94 mm × 8 mm) were fixed at both sides of the chamber in order to deposit the BCN films. The substrates (Ø24 mm × 9 mm) were polished, cleaned in acetone ultrasonically for 30 min, washed in deionized water, and dried under a nitrogen atmosphere.

During deposition, the chamber was evacuated to a base pressure of $3.5 \times 10^{-3}$ Pa and then Ar plasma sputtering was conducted to clean the substrates for 30 min at a bias voltage of $-1000$ V prior to deposition of the BCN films. The deposition pressure, bias voltage, substrate temperature, nitrogen flow ratio, and B₄C target power were kept at $3 \times 10^{-1}$ Pa, $-100$ V, 230 °C, 2 sccm, and 4 kW, respectively. The carbon contents in the BCN films were adjusted by changing the power applied to the graphite target from 0 to 6 kW.

The surface and cross-sectional morphologies of the BCN films were inspected using a JSM 7000F scanning electron microscope (SEM). The carbon content and chemical bonding information were determined from a PHI 5802 X-ray photoelectron spectrometer (XPS) with a monochromatized Al Kα source. The films were sputtered for 5 min by Ar ions to clean surface impurities before the XPS analysis. The microstructure of the BCN films was determined by D/max-3C X-ray diffraction and high-resolution transmission electron microscopy (JEM 2100F). The HR-TEM specimens were prepared by the following process. The deposited samples were first cut into disks (Ø24 mm × 0.3 mm) by electrical discharge machining and then grinded to 70 μm thickness using abrasive paper. The samples were finally thinned by using a TenuPol-5 electro polisher in a 5% perchloric acid alcohol solution with a piece of high density polyethylene (HDPE) paper covering the films in order to only expose one side for electropolishing. The hardness was measured on a micro-hardness tester equipped with a Vickers diamond indenter under a loading of 25 g. The friction coefficients were determined using a pin-on-disk tribometer under a loading of 1.25 N. GCr15 steel balls (C 0.95–1.05 wt.%, Cr 1.30–1.65 wt.%, Mn 0.20–0.40 wt.%, Si 0.15–0.35 wt.%, S ≤ 0.020 wt.%, P ≤ 0.027 wt.%, and Fe balanced) with hardness of HRC...
60–62 and diameter of 3 mm were used as the counterparts during the sliding tests at a sliding speed of 0.3 m/s at room temperature in air and 45% relative humidity. The surfaces after the tests were inspected by SEM (JSM 7000F). The profiles of the wear tracks were measured on a TALYSURF-4 mechanical profilometer and the volume wear rates were calculated by following formula:

\[ W = \frac{V}{Ls} \]

where \( V \) is the worn volume (mm\(^3\)), \( L \) is the load (N), and \( s \) is the sliding distance (m).

3. Results and discussion

Fig. 2 shows the composition of the BCN films deposited using different graphite target power. As the graphite target power increases, the carbon contents in the BCN films increase linearly reach a maximum value of 61.3 wt.% at 6 kW graphite target power. In contrast, the nitrogen and boron contents in the films decrease gradually with increasing graphite target power. The influence of the graphite target power on the composition of the BCN films can be explained by that the graphite target power increase leads to a higher reactive carbon atom density [17]. Consequently, more carbon atoms are incorporated into the films resulting in higher carbon contents but smaller relative boron and nitrogen concentrations.

The surface and cross-sectional SEM micrographs of the BCN films are shown in Fig. 3. The surface of the films is smooth and the particle size is about 100 nm. The BCN films with 61.3 wt.% carbon possess the finest particle size. The cross-sectional SEM micrograph shows that the BCN films are dense but not obviously defective and columnar structures can be observed.

Fig. 4 shows the C1s XPS spectra of the BCN films with different carbon contents. The intensity of C1s peak increases from 9500 to 18,000 counts per second (cps) as the carbon content increases from 26.9 wt.% to 61.3 wt.%. It implies that the total content of the C–X (X: C, N) chemical bonds increases with the carbon concentration. By means of Gaussian fitting, the C1s XPS spectra can be deconvoluted into three peaks centered at 284.6 eV, 286.2 eV, and 287.7 eV, which correspond to sp\(^2\)C–C, sp\(^2\)C–N and sp\(^3\)C–N bonds, respectively. Increase in the carbon content leads to higher intensities of all the three fitted peaks, suggesting that the sp\(^2\)C–C, sp\(^2\)C–N, and sp\(^3\)C–N bonds increase with carbon contents increase from 26.9 wt.% to 61.3 wt.%.

The XRD spectrum on the BCN films in Fig. 5 shows no crystalline peak except those originating from the high-speed steel substrate. Because of the very thin layer thickness and the very low XRD absorption coefficient of B, C and N elements, XRD with normal incidence is not suitable for structure analysis in our case. Hence, the BCN films deposited by RMS possess probably an amorphous structure. It has been suggested that the main reason for the BCN films being amorphous is that the thermodynamic driving force for nucleation or segregation is not strong enough in reactive magnetron sputtering [18].

High-resolution transmission electron microscopy (HR-TEM) is carried out to further determine the microstructure of the BCN films. As shown in HR-TEM picture Fig. 6 and the corresponding electron diffraction patterns acquired from the BCN films with different carbon contents, the BCN films have a random atomic arrangement as

![Fig. 4. C1s XPS spectra acquired from the BCN films with carbon contents of: (a) 26.9 wt.%, (b) 48.2 wt.%, and (c) 61.3 wt.%.](image)

![Fig. 5. X-ray diffraction patterns of the BCN films with various carbon contents deposited on high-speed steel (W18Cr4V) substrates.](image)
illustrated by the dim halo in the electron diffraction pattern. This evidence confirms that the BCN films have an amorphous structure. As the carbon content increases, the size of the amorphous clusters increases. It may indicate that the higher carbon content makes atomic clustering in the film easier.

Fig. 7 shows the hardness of the BCN films as a function of carbon content. The hardness values of the BCN films increase linearly with carbon concentrations from 26.9 wt.% to 61.3 wt.% reaching a maximum value of 18.2 GPa at 61.3 wt.% C. According to the XPS results, as the carbon concentrations increase, sp³C–N content increases obviously. The sp³C–N bonds have been theoretically predicted to give rise to super hardness in β-C₃N₄ materials [19]. Hence, the increase of the sp³C–N bond content can contribute to the hardness enhancement. Besides, the size increase in the amorphous clusters as the carbon content increases should also contribute to the hardness enhancement [18].

The friction coefficients measured from the BCN films with different carbon contents sliding against steel GCr15 balls are shown in Fig. 8. The average friction coefficients diminish gradually from 0.4 to 0.2 as the carbon concentration increases from 26.9 wt.% to 61.3 wt.% It indicates that a higher carbon concentration gives rise to a smaller friction coefficient. Decrease in the friction coefficients may be caused by the increase of sp³C–C and sp³C–N bonds (Fig. 4) which act as self-lubricating amorphous carbon and carbon nitride materials.

Fig. 9 shows the wear tracks on the BCN films with different carbon contents sliding against steel GCr15 balls. The wear track on the BCN films with 26.9 wt.% C is narrow and deep, and lots of scratches appear. It means that during the wear process, the steel ball is pressed into the films and the film is cut thereby leaving the scratches. In comparison, the wear track on the BCN films with 48.2 wt.% C is wider and shallower and the scratches become flat. It indicates that the indentation and cutting effect on the film is reduced when the carbon content increases. This should be attributed to the enhancement of the film hardness. The hardness of the BCN films with 48.2 wt.% C is about 15.2 GPa which is harder than that of the counterpart steel ball. Therefore, during the sliding process, the contact area of the steel ball is scratched to be flat [4] and the wear track on the film is wider and shallower. The scratches in the wear track of the BCN films with 61.3 wt.% C nearly disappear, and the boundary between the wear track and unbroken film surface becomes blur, but some white color small area appear in the wear track. By means of EDS, we find that the composition in this area is close to that of the high-speed steel substrate, suggesting that the film in this area has delaminated from the substrate during the sliding test. This is due to the relative weak adhesion between the film and substrate. During the sliding test, the film is extruded by cyclic stress and some low adhesive areas in the film produce micro-cracks. As sliding continues, the micro-cracks extend and connect to each other. Finally, the film in this area breaks off and the wearing destruction is similar to fatigue.

The volume wear rates measured from the BCN films are shown in Fig. 10. The volume wear rates gradually decrease from $2.2 \times 10^{-6}$ mm³/(Nm) to $0.9 \times 10^{-6}$ mm³/(Nm) when the carbon content increases from 26.9 wt.% to 61.3 wt.%, indicating that the BCN films with higher carbon contents show better wear resistance. The wear resistance enhancement
of the BCN films can be attributed to the hardness increase and friction coefficient reduction as the carbon content in the film increases.

4. Conclusion

The BCN thin films deposited by reactive magnetron sputtering have an amorphous structure in present study. The sp²C–C, sp²C–N and sp³C–N contents increase with the carbon concentration. Addition of carbon to the BCN films leads to higher film hardness but reduced friction coefficient. The tribological behavior of the BCN films determined from sliding tests against steel GCr15 balls changes gradually from micro-cutting to fatigue when the carbon content is increased. Enhancement of the film hardness and reduced friction coefficient are caused by the larger sp²C–C, sp²C–N and sp³C–N contents.

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References


Fig. 9. Wear tracks on the BCN films with carbon contents of (a) 26.9 wt.%, (b) 48.2 wt.%, and (c) 61.3 wt.% together with (d) EDS taken at the point a in image (c).

Fig. 10. Volume wear rates of the BCN films with various carbon contents.