Mechanical and tribological properties of B-C-N coatings sliding against different wood balls

Abstract: BCN coatings with different chemical compositions were prepared using RF magnetron sputtering via adjusting N₂ flow. The influence of N₂ flow on the bonding structure, mechanical and tribological properties of coating was studied. The structural analysis indicated the coexistence of B-N, B-C, and N-C bonds, suggesting the formation of a ternary BCN hybridization. The maximum Vickers hardness of 1614.7 HV was obtained at the low N₂ flow (5 sccm), whereas the adhesion strength of BCN coatings on 316L stainless steel was improved with an increase of N₂ flow. The friction behavior of BCN coatings sliding against different materials (acrylic, beech and lauan wood) was performed using ball-on-disk tribometer in air. The low friction coefficient was easier to obtain as sliding against hardwood i.e. acerbic balls. BCN-5 and BCN-10 coatings presented better wear resistance regardless of softwood or hardwood, whilst other two coatings were more suitable for mating softwood i.e. beech and lauan.

Keywords: BCN coating; Mechanical properties; Friction

1 Introduction

Ternary boron-carbide-nitride (B-C-N) coating attracts much attention due to its potential applications as tool or anti-wear material [1, 2]. Thus, researchers deposited B-C-N coatings using different deposition methods (physical or chemical deposition techniques) [2–5] to improve their mechanical and tribological properties. For instance, the BCN coatings deposited by co-sputtering B₄C and graphite targets showed better hardness and thermal stability than those deposited by sputtering B₄C in acetylene. Furthermore, the BCN coatings deposited with additional graphite target exhibited the lower friction coefficient (~0.1) than that of BCN coatings (~1.0) deposited without additional carbon source (graphite target or acetylene) [2].

Besides, researchers tried to control the chemical composition of B-C-N coatings to improve their mechanical and tribological properties [6–11]. For example, the increased boron content could improve the hardness as well as the residual stress of BCN coatings, while the lubrication of graphitized carbon transfer layer at 300 °C was critical to reduce the friction coefficient (~0.1) [6]. The increase of sp²-C-C and sp³-C-N bonds in coatings could enhance the hardness (11–18 GPa) and reduce the friction coefficient (μ = 0.4–0.2) of BCN coatings [7]. Similarly, the hardness of B-C-N coatings could be enhanced as the N content was below 10 at.% [10], while their hardness hardly changed once the N₂/Ar flow ratio was higher than 1/10 [8, 11]. Moreover, Ref. [9] found that the hardness of BCN coatings fluctuated in the range of 14.8–25.2 GPa as a function of nitrogen pressure (2.5–5.0 Pa). The highest hardness was obtained at the nitrogen pressure of 3.5 Pa due to a high fraction of C-B and sp³-N-C bonds as well as a low fraction of sp³-h-B-N bond.

In addition, the tribological properties of BCN coatings were sensitive to lubrication environment [12, 13]. For example, a low friction coefficient (0.25) and a low wear rate (1–2×10⁻⁷ mm³/Nm) of BCN coatings were obtained in the humidity of 25–75% RH, while a high wear rate of 1×10⁻⁵ mm³/Nm was obtained in dry air [12]. Zhou et al. [3] found that the low friction coefficient and wear rate of BCN coatings were attributed to the formation of H₂BO₃ film on friction surface in water lubrication. It is indicated that BCN coatings are suitable to be used in humid environment.

As we known, in the cutting process of wood, the friction between the tool (e.g. cutting edge, rake face and flank face) and wood is extremely high. Generally, the wear area of the cutting edge was used to evaluate the tool life [14]. However, because wood materials have unstable physical properties due to a heterogeneous internal structure, their friction behavior was dominated by loads, moisture, velocity and so on [15, 16]. Thus, finding a suitable cutting materials is needed. As stated above, BCN coatings are suit-
able to be used in humid environment and dry wood still contains about 10% moisture. In other words, BCN coatings are expected to have good tribological properties as sliding against woods. Moreover, it was reported that CBN coating lasted for 50% longer life than that of TiAlN coating as turning a nickel-based alloy [1].

Thus, in this work, we prepared BCN coatings using RF magnetron sputtering and investigated their mechanical and tribological properties sliding against different wood balls. The aim of this study is to reveal the friction behavior between BCN coatings and woods and to promote the BCN coatings application as woodworking tools.

2 Experimental details

2.1 Deposition of BCN coatings

The BCN coatings were simultaneously deposited on Si (100) wafers and 316L stainless steel substrates using magnetron sputtering system via adjusting N\textsubscript{2} flow. In order to obtain a stable glow, the B\textsubscript{4}C target was installed on RF target. The polished stainless steel disks (\(\Phi 30 \times 4\) mm\textsuperscript{2}) and Si (100) wafers were cleaned ultrasonically in deionizer water and ethanol for 20 min before being installed on substrate holder. When the chamber was evacuated to \(9 \times 10^{-4}\) Pa, substrates were cleaned with Ar plasma at a bias voltage of \(-100\) V for 30 min. The B\textsubscript{4}C target power and substrate temperature were set as 100 W and 100\(\circ\)C, separately. The BCN coatings were deposited for 1 hour at different N\textsubscript{2} flows (5 sccm, 10 sccm, 15 sccm and 20 sccm). According to N\textsubscript{2} flow, the BCN coatings were denoted as BCN-5, BCN-10, BCN-15 and BCN-20.

2.2 Characterization of BCN coatings

The bonding structures of BCN coatings were detected using X-ray photoelectron spectroscopy (XPS, AXIS Ultra-DLD), and the element content in coatings was measured at the same time. The Vickers hardness of coating was measured using a microhardness tester (HVS-1000, china) equipped with a 136\(\circ\) diamond probe. The applied load and holding time were set as 0.098 N and 10 s. The Vickers hardness was calculated according to the four-point measurement method. The coating adhesion to the 316L stainless steel substrate was defined in the scratch tester (WS-2005, Scratch Tester, China) equipped with a hemispherical diamond tip (\(R = 0.2\) mm). The applied load, sliding speed and wear track length were set to 20 N, 20 N/min and 3 mm, separately. The scratch test was repeated three times to ensure its reliability.

2.3 Tribological Properties of BCN coatings

The friction behavior of BCN coating sliding against different wood balls (e.g. acerbic, beech and lauan wood with a diameter of 8 mm) was investigated using a homemade ball-on-disc tribo-meter shown in Figure 1. During experiment, the friction forces of tribo-pairs were detected by a LMA-A-10 N load cell (Kyowa Co. LTD., Japan). The load cell voltage was measured by a DPM-700B strain amplifier (Kyowa Co. LTD., Japan) and recorded by NR-110/150 data collection system (Keyence Co. LTD., Japan) with a compatible computer. The resolution of the tribo-meter used in this study was 0.001. The applied load, sliding speed and sliding distance were set as follows: 3 N, 0.1 ms\textsuperscript{-1} and 300 m, separately. After friction test, the morphology of wear tracks was observed using an optical microscope.

Figure 1: Schematic diagram of ball-on-disc tribo-meter.

3 Results and discussion

3.1 Microstructure of BCN coatings

As seen in Table 1, the N content was non-proportional to the N\textsubscript{2} flow, but the boron content gradually decreased from 14.3 at.% to 72 at.% in addition, the carbon content slightly increased with the rise of high N\textsubscript{2} flows. Actually, the element contents in coating were determined synergistically by the following factors such as deposit temperature, target power, substrate bias and N\textsubscript{2}/Ar ratio. For example, V. Linss et al. [10] pointed out that the B/C ra-
tio in BCN coatings did not change with the N contents at low temperatures (≤ 100 °C) unless being deposited at elevated deposition temperature. Once the nitrogen plasma was saturated in chamber, neither increasing N$_2$ flow nor increasing N$_2$ pressure could cause regular change in nitrogen content [10, 17].

### Table 1: Chemical composition and Vickers hardness of BCN coatings.

| Coatings | B at.% | C at.% | N at.% | HV      |
|----------|--------|--------|--------|---------|
| BCN-5    | 14.3   | 76.8   | 8.9    | 1614.7±244.1 |
| BCN-10   | 10.6   | 81.6   | 7.8    | 1316.9±273.4  |
| BCN-15   | 7.3    | 85.9   | 6.8    | 1327.1±378.2  |
| BCN-20   | 7.2    | 82.3   | 10.5   | 1513.3±457.5  |

In order to reveal the chemical structures of BCN coatings, the corresponding B1s, C1s and N1s XPS spectra are illustrated in Figure 2. It is clear that the low intensity peaks are detected in B1s spectrum for BCN-5 and BCN-10 coatings (10.6~14.3 at.% B). The peak located at 186.5~186.9 eV were assigned to B-C bond (B$_x$C) [18], whilst that located at 189.3~189.5 eV were attributed to B-N bond. In addition, the B-O bond was detected at the binding energy of 191.5 eV. As compared with the former reports [8, 9, 13], the position of B1s peaks shifted to low binding energies, which was attributed to the high C concentration in coatings [19]. However, no obvious peaks were detected in B1s spectrum for BCN-15 and BCN-20 coatings due to their low boron contents. As seen in Figure 2(b), two deconvoluted peaks located at 398 eV and 400 eV were detected in N1s spectrum, which corresponded to N-B [19, 20] and N-C bonds [6], separately. According to the former reports [19, 20], the sp$^2$N-B and sp$^2$C-N bonds usually located at 397.3~398.0 eV and 400.5~401.5 eV, separately. Thus, the N-B and N-C bonds located at binding energy of 398 eV and 400 eV were sp$^2$ hybridization. In terms of C1s spectrum, three deconvoluted peaks were detected at different binding energies. According to the former reports, the binding energies of 284.2~284.6 eV, 285.4~285.9 eV and 286.4~286.9 eV were assigned to C-C (sp$^3$) [6, 8, 9], C-N (sp$^3$) [8, 9, 21] and C-N (sp$^3$) [9, 21], respectively. The binding energy usually shifted to high energy zone after N bonded with C atom because of the high electronegativity of N atom. Accordingly, as seen in Figure 2(c), the binding energy in the range of 284.4~284.8 eV corresponded to sp$^2$C-C, and the binding energies of 285.3~285.9 eV and 286.5~286.7 eV were assigned to sp$^3$C-N and sp$^3$C-N, separately. In addition, the appearance of C-O bond indicated that the surface of coatings was contaminated by oxygen from air. The coexistence of B-N, B-C, and N-C bonds in BCN coatings indicated the formation of a ternary B-C-N hybridization [9] and ternary composite materials [10].

### 3.2 Mechanical properties of BCN coatings

As seen in Table 1, the highest Vickers hardness of 1614.7 HV was obtained for BCN-5 coating, which attributed to its high B content. Similarly, Deng et al. [6] also pointed out that the high B content in BCN coating was helpful to increase its hardness. However, increased N$_2$ pressure [9] or N$_2$ flow [8, 19] also resulted in the decline of hardness for BCN coatings. That was because the increased N proportion could promote N atoms to preferentially bond with C, and resulting in decreased B-C and increased C-N bond content [8]. Based on the previous reports, the sp$^2$B-N and N-C bonds were verified as “soft” phases [22–24], whereas the B-C and sp$^3$N-C bonds were thought as “hard” phases [25, 26]. Here, BCN-10 coating only has sp$^2$C-C and sp$^3$B-N bonds without sp$^3$N-C in its C1s spectrum, resulting in the lowest hardness of 1316.9 HV.

The coating adhesion to the 316L stainless steel substrate was performed in the scratch tester as critical load was one of the more significant parameters. The acoustic emission signals and the corresponding friction force curves are illustrated in Figure 3. Usually, a sudden increase in acoustic emission signal means the appearance of tiny cracks on scratches, but the deposition defect or surface roughness also could cause a slight acoustic emission signal. Therefore, combining the friction force curve (e.g. slope or intensity) and scratch morphology is a more reasonable way to determine the critical load. As seen in Figure 3(a), the intensity of the acoustic emission signal suddenly increased after presenting a smooth straight line, and their friction force also fluctuated. The low critical loads (L$_{c1}$) were thought of crack initiation resistance [27, 28]. Accordingly, the low critical loads (L$_{c1}$) were determined, which increased from 1.5 N to 8.5 N with an increase of N$_2$ flows. In addition, the optical micrographs of scratches are illustrated in Figure 4s to determine the high critical loads (L$_{c2}$) corresponded to the appearance of flake crack or delamination on scratches [29]. As seen the amplification optical photographs in Figure 4(b), the scaly cracks appeared on their scratches at high critical loads. The corresponding acoustic emission signal and frictional force curves also presented some fluctuations in Figure 3. As a result, the L$_{c2}$ values were determined to be 13.0 N, 13.8 N, 13.2 N and 15.0 N, separately. Refs. [27, 28] pointed out that the scratch crack propagation resistance (CPRs) determined by critical loads could be used as quick qual-
Figure 2: XPS spectra of BCN coatings.
Figure 3: Acoustic emission signals and friction force for BCN films by a scratch tester.

Figure 4: Optical micrographs of scratches (a) and corresponding amplification optical photographs (b) by a scratch tester.

Figure 5: Friction behavior and mean friction coefficient of BCN coating as sliding against wood balls.

3.3 Tribological properties of BCN coatings

The friction behavior of BCN coatings is shown in Figure 5. As sliding against acerbic balls, the friction coefficient gradually increased in the whole sliding distance except BCN-5 coating. As sliding against beech balls, BCN-5 and BCN-10 coatings presented a steady coefficient of friction. In contrast, the friction coefficient increased dramatically with an increase of sliding distance for BCN-15 and BCN-20 coatings, implying the change of friction characteristics. As sliding against lauan balls, only BCN-5 coating kept a steady coefficient of friction within the whole sliding distance. As for the influence of mating balls, the mean stable friction coefficient (0.76~0.83) was obtained as sliding against acerbic balls in Figure 5(d), while the friction coefficient fluctuated greatly as sliding against other two balls (beech or lauan balls). In addition, the friction coefficient showed a great fluctuation. That was because the plant materials have a heterogeneous internal structure and exhibit high susceptibility to external conditions, which results from their unstable physical properties contrary to solids [15]. As seen in Figure 5d, the relatively high friction coefficient was obtained as sliding against softwood. It was a result of big contact deformation and high adhesion at the friction interface for softwood.

Optical images of wear scars for tribo-pairs are shown in Figures 6-9. As seen in Figure 6, smooth wear scars without any obvious scratches were observed regardless of mating balls. In addition, a small amount of debris adhered on the wear marks as sliding against acerbic and beech balls, whilst the debris accumulated at the edge of the wear mark as sliding against lauan balls. That result indicated the mild friction behavior occurred during their friction process with slight adhesion wear. In terms

\[ \text{CPRs} = L_{c_1}(L_{c_2} - L_{c_1}) \]
of BCN-10 coating, shallow abrasion marks were observed in Figure 7, even the scratches on the substrates have not been worn off. The wear track on BCN-10 coating as sliding against acerbic balls was narrower than those sliding against other two balls (beech and lauan balls). As seen in Figure 8a, some scratches obviously appeared on the wear track as sliding against acerbic balls, implying that the main wear mechanism was abrasive wear. In contrast, the abrasive wear was alleviated as sliding against other balls whilst appearing a small amount of wear debris adhesion (Figure 8b and 8c). Similarly, as seen in Figure 9a, scratches and wear debris were also observed on the wear tracks as sliding against acerbic balls, indicating that the abrasive wear and adhesion wear occurred during the friction process. For other two mating balls, more wear debris accumulated at the edge of the wear track (Figure 9b and 9c). Regarding the influence of wood species, softwoods (i.e. beech or lauan) were easier to produce tiny granular debris. In that case, the strong hygroscopicity of the granular debris produce large deformation to increase

Figure 6: Optical images of wear scars for BCN-5 coating sliding against different wood balls.
the real contact surface area, and then the adhesion between granular debris increase the friction force [15, 16]. This was one of the reasons to increase friction coefficient for softwood.

Refs. [27, 28] pointed out that the low critical load (Lc1) and CPRs could evaluate the crack initiation resistance and the persistence before a catastrophic failure occurs, separately. Though the critical loads and CPRs value of BCN-5 coating were the lowest as compared with other coatings, no fatigue cracks or delamination appeared on its wear tracks. That result was attributed to the high elasticity of wood which could effectively alleviate the stress concentration during friction testing. In terms of wood composition, some calcium magnesium potassium oxides are contained in wood, these oxides can play the role of abrasive particles during the friction process. As seen in Figures 6-9, smooth wear tracks were observed on BCN-5 and BCN-10 coating as sliding against acerbic balls, while serve abrasive wear was obtained for other two coatings, indicating that the wear resistance weakened with an in-

Figure 7: Optical images of wear scars for BCN-10 coating sliding against different wood balls.
crease of N$_2$ flows. However, the abrasive wear was alleviated as sliding against beech or lauan balls by comparison. It could be inferred that oxide particles mixed into tiny granular wood debris and then resulted in the loss of cutting function of oxides. Considering the XPS analysis, the reduced boron content weakened the B-N and B-C bonds as seen in Figure 2a. The absence of hard phase i.e. boron carbide phase in coatings was not conducive to improve the wear resistance of coatings. The excessively local wear of cutting edge resulted from chipping or abrasive wear was not conducive to improving the surface quality of wood processing [30]. As a result, it could be implied that a wide adaptability for BCN-5 and BCN-10 coatings as woodworking tools to cut hard or soft woods, whilst BCN-15 and BCN-20 coatings were suitable for cutting softwood.

Figure 8: Optical images of wear scars for BCN-15 coating sliding against different wood balls.
4 Conclusions

BCN coatings with low boron content were prepared using DC magnetron sputtering via adjusting \( N_2 \) flows. The influence of \( N_2 \) flows on structure, mechanical and tribological properties was studied. The following conclusions are obtained:

1. The boron content decreased from 14.3 at.% to 7.2 at.% with an increase of \( N_2 \) flows. The bonds such as B-C, C-N and B-N bonds were detected in BCN coating, indicating the formation of a ternary BCN hybridization.

2. The highest Vickers hardness of 1614.7 HV was obtained for BCN-5 coating. The critical loads and CPRs increased with an increase of \( N_2 \) flows in scratch testing, indicating the improved adhesion and crack propagation resistance of coatings.

3. In terms of friction behavior, the low friction coefficient was easier to obtain as sliding against hardwood (acerbic balls). BCN-5 and BCN-10 coatings presented better wear resistance regardless of softwood or hardwood, whilst other two coatings were more suitable for mating softwood.
Acknowledgements: This work was supported by the Jiangsu province college students practice and innovation training plan (Number 201910850003Y, 2018NFSU-PITP166) and Jiangsu university brand specialty construction projects (PPZY2015A087).

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