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Microstructure and tribological properties of cubic boron nitride films on Si_3N_4 inserts via boron-doped diamond buffer layers

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ABSTRACT

Cubic boron nitride (cBN) coatings were deposited on silicon nitride (Si_3N_4) cutting inserts through conductive boron-doped diamond (BDD) buffer layers in an electron cyclotron resonance microwave plasma chemical vapor deposition (ECR MPCVD) system. The adhesion and crystallinity of cBN coatings were systematically characterized, and the influence of doping level of BDD on the phase composition and microstructure of the cBN coatings were studied. The nano-indentation tests showed that the hardness and elastic modulus of the obtained cBN coatings were 78 GPa and 732 GPa, respectively. The tribological properties of the cBN coatings were evaluated by using a ball-on-disc tribometer with Si_3N_4 as the counterpart. The coefficient of the friction and the wear rate of the cBN coatings were estimated to be about 0.17 and 4.1×10^{-7} mm^3/N m, respectively, which are remarkably lower than those of titanium aluminum nitride (TiAlN) coatings widely used in machining ferrous metal. The results suggest that cBN/BDD coated Si_3N_4 inserts may have great potentials for advanced materials machining.

1. Introduction

Cubic boron nitride (cBN) is structurally analogous to diamond. Due to the strong covalent bonds and high atom density, both of them have outstanding physical and chemical properties, such as extreme hardness, excellent thermal conductivity, high chemical stability and low friction coefficient [1–3]. Compared with diamond, cBN has an even higher thermal stability, and oxidation and graphitization resistances [4,5]. While diamond burns at 600 °C and reacts with iron at elevated temperatures, cBN is chemically stable and does not react with ferrous materials at temperatures up to 1200 °C [6]. These properties along with maintaining its hardness up to 1000 °C pose cBN as an ideal material for machining steels and other ferrous materials. Thus far, cBN powders synthesized by high-pressure high-temperature (HPHT) methods are commercially available as abrasives, and they are also molded and cemented by metal binders to produce polycrystalline cBN (PcBN) cutting inserts [7–9]. Such PcBN tools have shown significantly improved processing efficiency as compared with the traditional cemented carbide (WC:Co) and high speed steel (HSS) tools. However, such cBN tools still suffer from the technical difficulties in cementing cBN powder into complex shapes and the high cost of the cBN powder and cementing, which motivate ion for thin film synthesis of cBN for tooling applications.

Various physical and chemical vapor deposition (PVD and CVD) techniques have been exploited to synthesize cBN coatings [1–3], and cBN coatings synthesized on cemented tungsten carbide (WC:Co) substrates for tooling applications have been reported [10,11]. It has been demonstrated that cBN deposited directly on WC was mechanically unstable, and transition layers, such as boron and boron-rich BN, were introduced to improve the adhesion and mechanical stability of cBN coatings [12,13]. Keunecke et al. reported that deposition of 1.2 μm-thick cBN films on WC inserts with TiN/BCN transition layers by radio-frequency diode sputtering, and the turning test showed that the cutting lifetime of the cBN coated inserts was prolonged as compared to the TiN and TiAlN coatings [14,15]. Due to the high compressive stress induced by intense ion bombardment in cBN deposition, the deposition of thick (>2 μm), adherent, and mechanically stable cBN coatings on cutting inserts remains a challenge. The development of fluorine-assisted CVD enabled the growth of high-quality, thick cBN films with significantly reduced residual stress [16,17]; and the cBN coatings were found to grow directly and epitaxially on diamond substrates, skipping the soft sp^2-BN incubation layer usually needed for cBN nucleation and improving the adhesion of cBN films greatly [18,19]. 2.8 μm-thick cBN films with high phase purity were synthesize on diamond-coated WC:Co inserts by using ECR microwave plasma CVD (MPCVD) with the assistance of fluorine chemistry [20]. Surface pretreatment of the WC:Co inserts by well-controlled chemical etching was required to remove the Co binder in the surface region of cutting inserts, so

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that the adhesion of diamond films could be enhanced. However, the high substrate temperatures during cBN deposition led to diffusion of Co from the bulk of insert to the diamond/insert interface, which resulted in the catalytic formation of graphite and deterioration of diamond adhesion [20,21]. The machining performance tests showed that the diamond–WC interface was the weak link in cBN/diamond coatings on WC inserts.

We report in this paper synthesis of cBN films on Si_3N_4 substrates through boron-doped diamond (BDD) buffer layers by fluorine-assisted ECR MPCVD. Si_3N_4 is one of the major ceramics for cutting tools due to its high hardness, outstanding thermo-mechanical and tribological properties and low fabricating cost [22]. In comparison with WC:Co substrates, Si_3N_4 has a lower mismatch of thermal expansion coefficient with that of diamond ($\alpha_{Si3N4} = 2.11 \times 10^{-6}\ K^{-1}$ and $\alpha_{WC} = 4.11 \times 10^{-6}\ K^{-1}$ versus $\alpha_{Diamond} = 0.8 \times 10^{-6}\ K^{-1}$) [23], and the degradation of diamond/substrate interface strength caused by Co diffusion can be avoided, which makes Si_3N_4 a remarkable substrate for high-quality diamond growth [24,25]. In this work, the effects of doping level of BDD films on the microstructure and composition of cBN/BDD coatings were investigated. The friction and wear performance of cBN/BDD coatings on Si_3N_4 (cBN/BDD/Si_3N_4) and the tribological behaviors of the reference TiAlN/WC were also evaluated.

2. Experimental

BDD films were deposited on Si_3N_4 cutting inserts (CN2000, ZCCCT, Co., Ltd, 12 × 12 mm) in a gas mixture of trimethylboron (TMB) in an ASTeX MPCVD system. The substrates were pretreated ultrasonically in diamond powder (~50 nm) suspension for 60 min to enhance the nucleation. TMB was diluted by H_2 to 0.1 vol.%, and the total gas flow rate was 300 sccm. The carbon to hydrogen ratio was maintained at 1%, and the boron to carbon ratio (B/C) was varied from 3000 to 12,000 ppm. For all samples, the microwave power was 1200 W, the substrate temperature was kept at 760 °C, the reactive pressure was 30 Torr, and the growth duration was 12 h.

Cubic BN films were deposited on the BDD-coated Si_3N_4 inserts in the ASTeX ECR MPCVD system in a gas mixture of $BF_3 + N_2 + Ar + He + H_2$. The cBN coatings on BDD films with B/C ratios of 3000, 7000 and 12,000 ppm were named as Samples 1, 2 and 3, respectively, in this paper. The gas flow rates of BF_3, N_2, Ar, He and H_2 were maintained at 10, 50, 10, 131 and 2.5 sccm respectively. In the deposition chamber, the Si_3N_4 insert was mounted on a Mo holder. A pyrolytic BN was used to cover the Mo holder and expose only the insert to plasma during deposition. The deposition pressure and substrate temperature were kept at 2×10^{-3} Torr and 900 °C, respectively. A DC bias of -40 V was applied to the substrate during deposition, and the growth time was 8 h. The deposition was performed under the optimized conditions based on our previous works [18–20]. A microwave power of 1400 W was employed to generate ECR plasma; and the high microwave power could enhance the plasma density and ionization degree, enabling cBN deposition at reduced bias voltages. Moreover, the growth rate and crystallinity of cBN could also be improved, similar to the deposition of diamond/β-SiC composite films by conventional MPCVD [26,27].

The surface and cross-section morphologies of BDD and cBN coatings were observed by scanning electron microscopy (SEM, PHILIPS XL30), and the elemental compositions of cBN films were studied by using energy dispersive X-ray spectroscopy (EDX) attached to the SEM. The phase compositions of BDD and cBN films were characterized by visible and UV Raman spectroscopy (Renishaw inVia) with excitation wavelength of 514 and 244 nm. Small-angle X-ray diffraction (XRD, Rigaku SmartLab) was carried out to investigate the microstructure, grain size, and stress of cBN films. The resistivity of the BDD films was detected by a 4-point probe method.

The mechanical and tribological properties of cBN coatings were investigated in comparison with those of commercial TiAlN coatings on WC:Co substrates. The hardness and elastic modulus of the cBN coating were measured by nanoindentation (Nano Indenter XP). The tribological behaviors of the coatings were investigated using a ball-on-disc (BOD) tribometer (HT1000). Si_3N_4 balls (HV 1600) with a radius of 3 mm were used as the friction counterpart. The temperature and relative humidity were kept between 21–25 °C and 38–55%, respectively. The sliding speed of 0.2 m/s was preset at a load of 5 N. The Si_3N_4 ball slid on a circular track with a radius of 2 mm, and the total sliding distance was 2000 m. The cross-section area of wear tracks on the coating was determined with a non-contact optical profilometer (Nanomap 500LS).

3. Result and discussion

3.1. Microstructure of cBN coatings

The SEM surface morphologies of the BDD films deposited with B/C ratios of 3000, 7000, and 12,000 ppm are shown in Fig. 1(a)–(c), respectively. It can be seen that all films are polycrystalline with the facets of diamond grains well resolved. More small diamond grains of multiple twinning structures were formed on the surfaces of BDD films grown with an elevated B/C ratio. The Raman spectra of the corresponding BDD films are presented in Fig. 1(d). A sharp diamond peak located at about 1339 cm^{-1} was revealed for the film prepared with the B/C ratio of 3000 ppm, indicating a high crystallinity of the film. The diamond peak shifted from 1339 to 1329 cm^{-1} as the B/C ratio increased from 3000 to 12,000 ppm, and the downshift could be attributed to the Fano effect caused by boron doping [28,29]. With the increase of B/C ratio, the intensity of G peak at 1580 cm^{-1} increased, which suggested an increased sp^2 carbon phase in the BDD films of higher boron doping levels. Moreover, for the film deposited with the B/C ratio of 12,000 ppm, broad peaks at 500 and 1220 cm^{-1} appeared, which are also due to the Fano effect as reported previously [28,29]. The electrical resistivity of the BDD films was revealed to decrease with the increase of B/C ratios. At the B/C ratio of 3000, 7000 and 12,000 ppm, the resistivity of BDD films was measured to be about 0.75, 0.16 and 0.09 Ω cm, respectively. The boron doping of diamond buffer layer results in the improvement of electrical conductivity, which is critical for the application of substrate bias for cBN deposition.

Fig. 2(a)–(c) depicts the SEM surface morphologies of the samples after cBN deposition on the BDD films prepared with the B/C ratios of 3000 (Sample 1), 7000 (Sample 2) and 12,000 ppm (Sample 3), respectively, and the inserts show the EDX spectra of the corresponding films. For Sample 1, the facets of diamond grains could still be clearly distinguished, and the EDX spectrum revealed only a carbon signal, which indicated that no cBN film was deposited atop the BDD layer. For Sample 2, a thin film was formed on the BDD film. The EDX spectrum showed boron and nitrogen signals in addition to carbon, which suggested that the cBN film partly covered the underlying BDD layer. In contrast to the above two samples, only boron and nitrogen were detected in EDX spectrum of Sample 3, implying a full coverage of the BDD layer by the cBN coating. The SEM morphology also confirmed the uniform deposition of a continuous BN film, as shown in Fig. 2(c). The cross-sectional SEM image in Fig. 2(d) shows that a 2.2 μm-thick cBN film was obtained on Si_3N_4 cutting inserts precoated with a 4 μm-thick BDD layer.

Fig. 3(a) shows the UV Raman spectra of Samples 1–3. Only diamond and graphitic carbon peaks located at 1332 and 1580 cm^{-1} respectively were observed for Samples 1 and 2, and these two spectra were almost the same as those acquired from the corresponding BDD substrates as shown in Fig. 1(d). Nevertheless, two additional peaks located at 1045 and 1305 cm^{-1} were revealed for Sample 3, which were assigned to the transverse (TO) and longitudinal optical (LO) modes of cBN [30]. Small-angle XRD was carried out to further verify the growth of cBN film in Sample 3, as shown in Fig. 3(b). The incident X-ray angle α was set at 0.3° and diffraction pattern was taken by 2θ continuous mode