Growth and mechanical properties of diamond films on cemented carbide with buffer layers

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ABSTRACT

The main hindrance to applications of diamond coatings on cemented carbide cutting tools is poor adhesion between diamond films and the substrates, caused mainly by Co acting as a catalyst for the formation of graphite during the growth of the diamond films. The buffer-layer technique is commonly used to reduce the elemental diffusion or residual stress in the interface between the film and substrate. In this paper, four kinks of buffer layers, namely TiN, CrN, TiC, and SiN, were applied to (111)-textured diamond films grown on mirror-polished cemented carbide substrates using the hot-filament chemical vapor deposition method. The adhesion strengths of different samples are measured by Vickers hardness tests and compared to show the different effects of the buffer layers. The sample with an 800-nm-thick CrN layer and processed by 10-min chemical etching has the best adhesion among the four buffer layers.

1. Introduction

Diamond films are applied on cemented carbide cutting tools due to their outstanding physical and chemical properties, such as the highest hardness, low friction coefficient, chemical inertness, and wear resistance [1,2]. However, these applications have been hindered since the binder cobalt, which tends to diffuse from the cemented carbide during the growth of the diamond films, promotes the formation of interfacial graphite layer that remarkably reduces the adhesion between the films and substrates [3]. Therefore, several kinds of pretreatment procedures have been proposed to eliminate or reduce the negative effects of Co, including one-step chemical etching, two-step chemical etching, formation of stable Co compounds, and deposition of buffer layers.

The procedures of chemical etching can dramatically remove Co binder at surfaces of cemented carbide tools. In one-step chemical etching, the cemented carbide tools are ultrasonic washed in single or mixed inorganic acid, such as HCl and HNO_3, for different time. In two-step chemical etching, Murakami solution ($K_3Fe(CN)_6$:KOH:H_2O = 1:1:10) is used first to erode WC grains on micron level, and then aqua regia (HNO_3:HCl = 1:3) is used to dissolve the remained Co. Despite of one-step or two-step, a fragile layer with low concentrations of Co could not be avoided on the surface of substrate owing to the outflow of Co, thus is subject to fracture or delamination [4] when the diamond-coated tools are in use.

Improvements on adhesion could also be achieved with substrate pretreatments to form stable Co compounds (such as borides or silicides),

which decrease the Co vapor pressure and mitigate other influences originated from the mobile Co phase [5]. Another pretreatment for improvements on adhesion is using various intermediate layers, ranging from metals to superhard ceramics, for example, tungsten [6] and aluminum [7], and carbide and nitride layers such as TiN, Ti(C,N) and CrN [8,9], whose purpose is to reduce the diffusion of binder cobalt.

For the buffer-layer methods the adhesion strength of the buffer layers to substrates and to diamond is an important factor of the performance of the diamond coatings. In this paper, we have synthesized diamond-coated cemented carbide inserts with and without buffer layers, and compared the effects of the buffer layers on the performance of the diamond coatings. TiN, CrN, TiC and SiN are selected for the buffer layers.

2. Experimental details

Φ10 mm × 2 mm WC–6 wt.% Co inserts (obtained from a sales agent of Sandvik Coromant) were used as the substrates. Before deposition of the buffer layers, the inserts were successively polished by diamond powder suspension with different particle sizes until a mirror surface was formed. To reduce the catalytic effect of Co binder and to improve the nucleation rate of diamond films, each sample was pretreated with chemical etching before the introduction of buffer layers and subsequent ultrasonic seeding.

The Co binder was ultrasonically etched by mixed acids (HCl(36%):HNO_3(68%):H_2O = 1:1:1) for 10 min firstly. The samples were then cleaned in deionized water and ethanol. Afterwards, the buffer layers (TiN, CrN, TiC SiN) were deposited with direct current (DC) or radio frequency (RF) magnetron sputtering. All the substrates were

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heated to 300 °C. After the depositions, the thicknesses of the buffer layers were about 800 nm as measured with a probe profilometer. Table I shows the pretreatments of each sample. Before diamond coating, all the samples were ultrasonically treated in diamond powder suspension for 1 h to improve the nucleation rate of diamond films. The deposition of diamond films was performed with a hot filament chemical vapor deposition (HFCVD) system (sp³ Diamond Technologies Model 655) with CH_4 (2000 sccm) and H_2 (80 sccm). The substrate's temperature is about 750 °C ± 30 °C and the filament's temperature is up to 2250 °C. After 10-h deposition, the thickness of diamond films was about 3 μm.

Grazing incidence X-ray diffraction (XRD, D/MAX2500, Cu Kα radiation, 40 kV and 25 mA) was adopted to identify the crystal structure of the buffer layers and the diamond films. XRD patterns were acquired in the 2θ range of 20–80°, using a grazing incidence angle geometry with ω = 0.5° (scan step size = 0.02°, time per step = 1.2 s). The phase particularity of the diamond films was characterized by a confocal Raman spectroscopy (INVIA, Renishaw plc, 633 nm). The surface morphology of the films was observed by field-emission scanning electron microscopy (SEM, Quanta FEG-250, 10 kV). The hardness and elastic modulus of the diamond films were obtained from in-situ nanomechanical testing system (Tribo indenter, Hysitror. Co. Ltd, nano-indentation mode). The adhesion of the diamond films on the substrates was determined by Vickers hardness indentation test (load = 9.8 N, holding time = 10 s).

3. Results and discussions

3.1. Grazing incidence XRD test

Fig. 1 shows the XRD patterns of the four buffer layers (TiN, CrN, TiC, and SiN), and the diamond films deposited on the four buffer layers, respectively. The figure shows that the films deposited on these four buffer layers are of diamond phases and, from the relative intensities of the diffraction peaks, the diamond films contain well-grown (111) plane, which corresponds to the scattering angle 2θ = 45°.

In Fig. 1(a), the (111), (200) and (220) diffraction peaks of TiN are clearly detected at 2θ = 36.78°, 42.6°, 62.0°, respectively, and (111) is the preferred orientation. After the diamond film was deposited, a new peak was found at 39.7° and is confirmed to be for the (101) plane of $TiN_{0.3}$ (PDF no. 41-1352) [10]. During the deposition of the diamond films, the temperature of the substrate increased to nearly 750 °C and the binder cobalt might migrate to the interface between the substrate and TiN layer, or even enter the TiN layer. The diffused Co could form CoN with N, which causes elemental segregation in the TiN layer and the appearance of non-stoichiometric compounds like $TiN_{0.3}$. Similarly, a tiny mismatch between the XRD pattern of the TiC in this experiment and the standard card of TiC (PDF no. 32-1383), also appears in the XRD pattern of the TiC films with and without a diamond layer. From Fig. 1(c), the diffraction peak of the "TiC" without diamond at 2θ = 36.21° corresponds to the (111) plane of TiC. This scattering angle is located between 35.9° (the (111) plane of TiC (PDF no. 32-1383)) and 36.85° (the (111) plane of $(W,Ti)C_{1-x}$ (PDF no.20 − 1309)). This tiny mismatch may be resulted from thermal reactions between TiC and WC as the deposition temperature of the TiC is 300 °C, high enough to activate atomic diffusion and chemical reactions.

As distinct from the TiN and TiC buffer layers, the CrN buffer layer might have an apparent reaction with C during the diamond deposition process since additional peaks of Cr_3C_2 [11] appear in the XRD pattern, as shown in Fig. 1(b). In Fig. 1(d), apart from the diffraction peaks of WC, no peak of SiN exists, neither before nor after diamond deposition, suggesting that the SiN buffer layer fabricated in this experiment is amorphous instead of crystalline. Because the chemical activity of Si is inferior to Ti and Cr, no reactions should arise between SiN and Co, WC, as well as C.

3.2. SEM and Raman test

The surface morphology of Samples 2, 3, 4 and 5 are shown in Fig. 2(a, b, c, d), which indicates that the diamond deposition has nucleated effectively on the four kinds of buffer layers. Unlike typical pyramid-shaped diamond grains mentioned in other articles [11,12], rice-shaped diamond grains were observed with extremely small grain sizes, about 50–100 nm. The small grains should lead to a large content of grain boundaries in the diamond films.

The Raman shift of Sample 2 is shown in Fig. 2(e). In order to obtain more information about the quality of the diamond films from the Raman spectra, a data reduction process was implemented. However, the first-order diamond Raman band at 1332 cm^{-1} is absent in the spectra. This may be originated from that the diamond Raman band is covered by other non-diamond Raman band [13], like the broad band at 1340 cm^{-1}. According to the rules of the reduction procedure, i.e. Gaussian fitting, a base line including luminescence contribution was removed and four main bands contribute to the Raman spectra of diamond films [14,15]. The two broad bands at around 1340 cm^{-1} and 1560 cm^{-1} are considered as the disorder (D) and graphite (G) bands of graphite, respectively. Besides, two relatively narrow peaks also exist at around 1200 cm^{-1} and 1450 cm^{-1}. The Raman shifts of Samples 3, 4 and 5 are also analyzed using the same method and are shown in the inserts of Fig. 2(b, c, d). Due to the existence of a large quantity of grain boundaries in the nanocrystalline diamond, these two bands always appeared simultaneously, which are assigned to trans-poly-acetylene lying in grain boundaries in low-quality CVD diamond film [16]. The origin of such trans-poly-acetylene must be related to the deposition mechanism.

Firstly, the well-grown and dense buffer layers (nitride and carbide) could significantly prevent the diffusion of Co from the substrates to the diamond films during the diamond deposition [17,18]. The effective reduction of the diffusion of Co could eliminate the negative influence of Co. Secondly, the location of the G-band is around 1560 cm^{-1} and I_D/I_G, the intensity ratio of D-band and G-band, is 1.274, suggesting that the state of graphite is NC-graphite [19], which is the graphite phase existing in low-quality nano-diamond films and is not induced by Co. The I_D/I_G of Samples 3, 4 and 5 are 1.278, 1467 and 1.487 respectively. For the diamond films with different buffer layers, the relationship of I_D/I_G is as follows:

$$I_D/I_G(\text{TiN}) \approx I_D/I_G(\text{CrN}) < I_D/I_G(\text{TiC}) < I_D/I_G(\text{SiN}).$$

According to the literature [19], while the state of graphite is NC-graphite in the diamond films, the larger the value of I_D/I_G is, the smaller the content of sp³ phase is and the larger the content of sp² phase is. Since NC-graphite is the main sp² phase and diamond is the sp³ phase, the relationship of the values of I_D/I_G for these four buffer layers implies that the content of diamond phase may be the highest in the diamond films with TiN and CrN buffer layers, less with TiC, and the lowest with SiN. Diamond films containing different sp² and sp³ contents with different buffer layers may have different behaviors during mechanical tests and service.

Table I
Substrate pretreatment before diamond deposition.

Sample	Pretreatment	Deposition conditions of buffer layers
1	Chemical etching (CE) 10 min	–
2	CE 10 min + 800 nm TiN layer	Ti target (DC), Ar + N_2 (0.5 Pa), sputtering
3	CE 10 min + 800 nm CrN layer	Cr target (DC), Ar + N_2 (0.8 Pa), sputtering
4	CE 10 min + 800 nm TiC layer	Ti target (DC), C target (RF), Ar (0.6 Pa), co-sputtering
5	CE 10 min + 800 nm SiN layer	Si target (RF), Ar + N_2 (0.5 Pa), sputtering