

Preparation and Cutting Performance of Boron-Doped Diamond Coating on Cemented Carbide Cutting Tools with High Cobalt Content

Zhaozhi Liu, Feng Xu, Junhua Xu, Xiaolong Tang, Ying Liu, Dunwen Zuo

Abstract—Chemical vapor deposition (CVD) diamond coated cutting tool has excellent cutting performance, it is the most ideal tool for the processing of nonferrous metals and alloys, composites, nonmetallic materials and other difficult-to-machine materials efficiently and accurately. Depositing CVD diamond coating on the cemented carbide with high cobalt content can improve its toughness and strength, therefore, it is very important to research on the preparation technology and cutting properties of CVD diamond coated cemented carbide cutting tool with high cobalt content. The preparation technology of boron-doped diamond (BDD) coating has been studied and the coated drills were prepared. BDD coating were deposited on the drills by using the optimized parameters and the SEM results show that there are no cracks or collapses in the coating. Cutting tests with the prepared drills against the silumin and aluminum base printed circuit board (PCB) have been studied. The results show that the wear amount of the coated drill is small and the machined surface has a better precision. The coating does not come off during the test, which shows good adhesion and cutting performance of the drill.

Keywords—Cemented carbide with high cobalt content, CVD boron-doped diamond, cutting test, drill.

I. INTRODUCTION

WITH the continuous development of the automotive, military, electronics and aerospace industries, high-silicon aluminum alloys, composites, titanium alloys, fiber-reinforced plastic and other difficult-to-cut materials have more and more applications [1]. Practice shows, in the high-speed cutting of these difficult-to-cut materials, high-speed steel and cemented carbide tools wear seriously, so there is an urgent need for less wear, longer service life, higher precision new tools. Diamond coating has a vast tool application in cutting difficult-to-cut materials due to its outstanding physical and chemical properties, such as the highest hardness, low friction coefficient, chemical inertness and wear resistance [2]. The well-adherent diamond coating is competent for machining these difficult-to-cut with high

efficiency and precision, which will prolong cutting tool life and improve production efficiency remarkably [3]-[6].

Substrate materials have a very significant impact on the diamond nucleation, growth, morphology, even the structure and membrane-based binding force. Cemented carbide is currently the most widely used research tool material which has broad application prospects. By controlling the content of the cobalt binder, tools of different toughness and strength can be obtained. The cemented carbide tools may also have complex shapes, such as drills, cutters, and be widely applied in many fields. Co binder phase in the cemented carbide tool material is detrimental to diamond nucleation and growth in the CVD process, which will result in the catalytic formation of graphite. Therefore, the pretreatment procedures prior to diamond deposition are necessary to eliminate or reduce the negative effect of Co binder in tool substrate. Among those pretreatment procedures, selective removal of Co on cemented carbide tool surface by chemical etching is commonly used in industry. At the same time, the thermal expansion coefficient of WC is different from that of diamond, after coating deposition the thermal stress will reduce the adhesion strength.

At present, cemented carbide materials with Co binder less than 6 wt.% are usually selected as substrates for diamond film. The pretreatment methods used currently are focused on the cemented carbide substrate with low Co content. As the toughness and strength of cutting tools increase with the increase of Co content, which improve the cutting performances of the tools. The cutting tool with high strength matrix and high wear resistant coating is more suitable for machining difficult-to-cut composite materials [7], [8]. The boron-doped diamond (BDD) is prepared by a dynamic introduction of boron during the growth process. The introduction of the boron atoms in the diamond can make the diamond become semiconductor material even conductor, and therefore the BDD film has been widely used and researched in the field of microelectronics and electrochemistry [9]-[11] compared to the application in the tool [12]-[15]. Studies have shown that an appropriate amount of boron dopant can refine diamond grains, reduce film stress, improve film quality and so on [16]. In this paper, the BDD diamond films were deposited on cemented carbide drills with high Co content for the first time and the prepared drills proved to have better cutting performance than those original drills.

II. EXPERIMENT DETAILS

Φ3.2 mm WC-10 wt.% Co drills (YG330) were used as the

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substrates. Before deposition, pretreatments were done to reduce the catalytic effect of Co binder on the nucleation during the growth of film. The pretreatments include abrading, chemical etching and seeding. Chemical etching procedure is a two-step process, in which Murakami solution ($K_3Fe(CN)_6$: $KOH:H_2O=1:1:10$) was used to attack the cemented carbide for 30 min and then the remained Co was removed with aqua regia ($HNO_3:HCl=1:3$) for 2-4 min. The two-step method handles only part of the drill to maintain the strength of the drill shank. Then, the samples were cleaned ultrasonically in deionized water. In the end, the seeding process lasts for 20 min in the diamond acetone suspension.

The boron-doped diamond coating was deposited on the cemented carbide drills in the home made hot filament chemical vapor deposition (HFCVD) system with CH_4 and H_2 as reacting gas, the boron dopant is B_2H_6 . The total gas flow rate was about 400 sccm and the flow rate of CH_4 gas was kept at 8 sccm at the diamond nucleation stage and 4 sccm at the diamond growth stage. The B/C ratio is 3000 ppm. The working pressure was kept at 2.5 kPa in the reacting chamber. Tungsten filament temperature was in the range of 2100-2300°C and the substrate temperature was about 800°C measured with a K-type thermocouple. Deposition time lasted about 5 hours.

The phase composition of the deposited diamond films was characterized by LABRAM-HR Raman spectroscopy. The light source was an argon ion laser with a wavelength of 514.5 nm. The surface morphology was determined using SEM system (S3400).

In this paper Rogers 6010 aluminum base microwave PCB is selected as the work piece. Recently, the aluminum base micro-wave PCB is used as a high frequency microwave communication device, which is composed of resin, reinforced materials, copper foil and aluminum base. The microwave PCB has wide application foreground in communication, medical treatment, military, instrument and other fields for its a series of excellent performances [17]. The micro-wave PCB needs high machining accuracy and surface quality. The dielectric layer of the microwave PCB has two phase—the polytetrafluoroethylene (PTFE) and ceramic powder. It is a typical difficult-to-machine material because the ceramic particle bonded with PTFE has high strength and hardness [18].

In our drilling experiment, traditional drills and BDD drills are used to machine aluminum base microwave PCB (Rogers 6010, 75mm×90mm) and Al-Si composite materials (silicon content of 50%) respectively. The diameter of the drill was 3.2mm and BDD drill was prepared as mentioned above. The machine tool (Z5125) is vertical drilling made by Dahe tool factory. The cutting speed is 1250 r/min and feed rate is 0.02 mm/r. First we drilled through-holes with depth of 5 mm on the microwave PCB; then used the same drill machined blind-holes on the aluminum-silicon composites with depth of 3 mm.

III. RESULTS AND DISCUSSION

The chemical quality of as-deposited boron-doped diamond film is evaluated by Raman spectroscopy. The Raman spectrum of the BDD film is shown in Fig. 1.

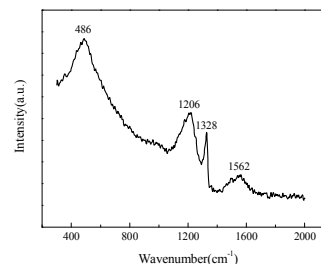


Fig. 1 Raman spectra of the BDD films

Sharp peak at 1332 cm^{-1} corresponded to the sp^3 bonding of diamond can be detected from undoped diamond films, indicating the high phase-purity polycrystalline diamond. As for boron-doped diamond films, the diamond characteristic peak at 1332 cm^{-1} downshifts to 1328 cm^{-1} due to the slightly boron doping, and peak at 1562 cm^{-1} is attributed to the graphitic carbon (G peak). This shift, as well as the specific asymmetric peak shape is due to the Fano interaction [19]. The broad bands around 486 cm^{-1} and 1206 cm^{-1} may well be associated with the actual boron incorporation in the lattice. Their position agrees well with the two maxima of the phonon density of states (PDOS) of diamond [20].

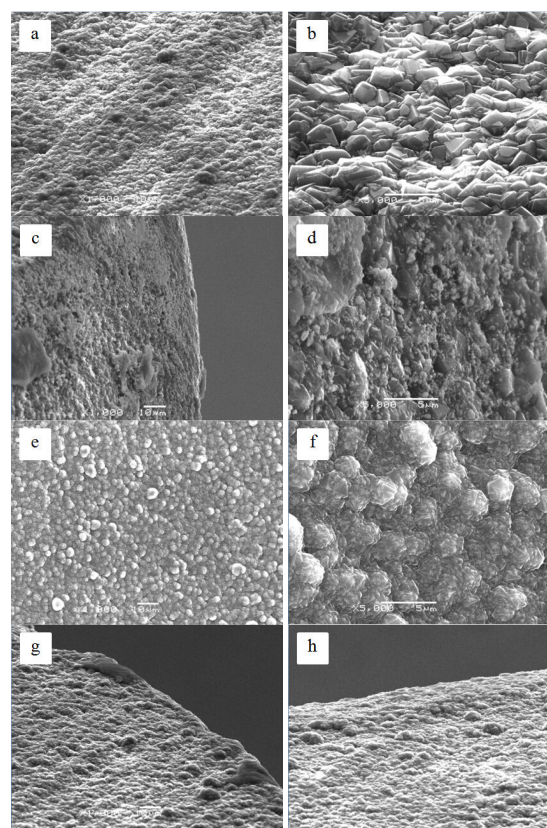


Fig. 2 SEM micrograph images of the boron-doped diamond deposited on the WC-Co drills: (a) main edge flank ; (b) enlarged view of (a); (c) minor cutting edge; (d) enlarged view of (c); (e) spiral groove; (f) enlarged view of (e); (g) main cutting edge; (h) enlarged view of (g)

The morphology of as-deposited boron-doped diamond films examined by SEM is compared in Fig. 2. All various parts of

diamond films exhibit faceted crystallites. Figs. 2 (a), (b) show a continuous boron-doped diamond film with well-defined polycrystalline facets due to the $\langle 100 \rangle \langle 111 \rangle$ texture on the surface of the main edge flank, it is estimates that the grains size were about 1-2 μm ; The diamond on the minor cutting edge is also have good quality and prominent angular particles with a layer of the impurities covering on the surface; Diamond particles on central spiral groove are spherical-crystals clustered together. It can be seen clearly that these small grains size were about 1 μm under high magnification; Diamond films on the main cutting edge and chisel have no cracks or coating peeling phenomenon.

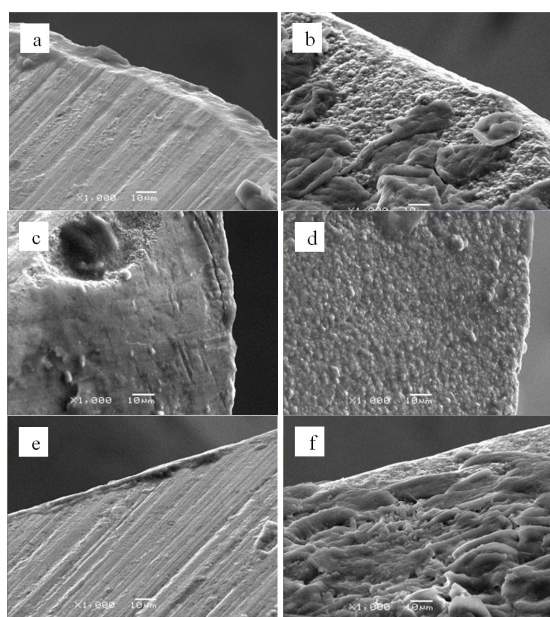


Fig. 3 SEM micrograph images of worn samples after the machining test: (a) original drill, main cutting edge; (b) BDD drill, main cutting edge; (c) original drill, minor cutting edge; (d) BDD drill, minor cutting edge; (e) original drill, chisel edge; (f) BDD drill, chisel edge

The above SEM views show the wear morphology of the drills after drilling 25 holes. Figs. 3 (a), (b) show the main cutting edge of the original drill wears severely, for the BDD drill some residue is left on the cutting edge after the drilling and some grains is worn. There are also some grease and impurities on flank; minor cutting edge flank of the original drill is covered with residue and damaged someplace, whereas the BDD drill exhibit good adhesion and no damage or wear found; Figs. 3 (e), (f) show the wear of the chisel edges have little difference.

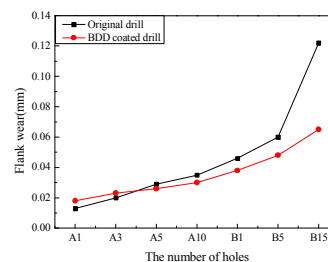


Fig. 4 Relationship curve between the number of holes and the flank wear after drilling

Fig. 4 shows the relationship curve between the number of drilled holes and its flank wear. A1-A10 denote the first 1-10 holes drilled on aluminum base microwave PCB, B1-B15 represent the next 1-15 holes drilled on the Al-Si composites.

The wear of the two kinds of drills increase relatively flat when drilling PCB whereas increase dramatically when drilling composites. When drilling the first three holes the amount of wear of the coated drill is slightly higher than the original drill, which was due to the rough surface of the coating; then from the fifth hole to the end of the experiment, the amount of wear of the BDD drills is smaller than the original drills and the coated drills show better wear resistance.

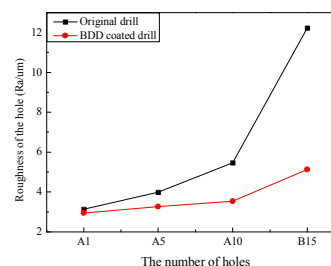


Fig. 5 The relationship curve between the roughness and the number of holes drilled

The relationship between roughness and the number of drilled holes are illustrated in Fig. 5. The view shows that when drilling the first hole, the roughness is almost the same, whereas with the increase in the number of the drilled holes, the surface roughness also increases greatly and compared with the BDD drill, the roughness of the hole drilled by the original drill increases rapidly, particularly when machining the aluminum-silicon composite materials. Overall, the roughness of holes drilled by the coated drills is smaller than the holes drilled by the original drills. This is because an appropriate amount of boron in the diamond improves the adhesion of diamond coatings, refines grains and reduces the surface roughness. Meanwhile, the boron atoms can stabilize the surface of the film and enhance oxidation resistance, heat resistance and mechanical properties of the coating. These reasons explain the excellent drilling performance of the boron-doped diamond drills.

REFERENCES

- [1] Gomez H, Durham D, Xiao X, et al, "Adhesion analysis and dry machining performance of CVD diamond coatings deposited on surface

- modified WC-Co turning inserts," *J. Mater. Process. Technol.*, vol. 212, no. 2, pp. 523–533, Feb. 2012.
- [2] Xu F, Xu J H, Yuen M F, et al, "Adhesion improvement of diamond coatings on cemented carbide with high cobalt content using PVD interlayer," *Diamond Relat. Mater.*, vol. 34, pp. 70–75, Apr. 2013.
- [3] Roy P, Sarangi S K, Ghosh A, Chattopadhyay A K, "Machinability study of pure aluminum and Al-12% Si alloys against uncoated and coated carbide inserts," *Int. J. Refract. Met. Hard Mater.*, vol. 27, no. 3, pp. 535–544, May. 2009.
- [4] Sun F H, Zhang Z M, Chen M, Shen H S, "Improvement of adhesive strength and surface roughness of diamond films on Co-cemented tungsten carbide tools," *Diamond Relat. Mater.*, vol. 12, no. 3-7, pp. 711–718, Mar-Jul. 2003.
- [5] Zhang D, Shen B, Sun F, "Study on tribological behavior and cutting performance of CVD diamond and DLC films on Co-cemented tungsten carbide substrates," *Appl. Surf. Sci.*, vol. 256, no. 8, pp. 2479–2489, Feb. 2010.
- [6] Sarangi S K, Chattopadhyay A, Chattopadhyay A K, "Effect of pretreatment methods and chamber pressure on morphology, quality and adhesion of HFCVD diamond coating on cemented carbide inserts," *Appl. Surf. Sci.*, vol. 254, no. 13, pp. 3721–3733, Apr. 2008.
- [7] Y. Jamal, Sheikh-Ahmad, *Machining of Polymer Composites*. New York: Springer-Verlag, 2009, ch. 4.
- [8] Tang Y, Li Y S, Yang Q, et al. "Deposition and characterization of diamond coatings on WC-Co cutting tools with W/Al interlayer," *Diamond Relat. Mater.*, vol. 19, pp 496-499, May. 2010.
- [9] Juang Y, Nurhayati E, Huang C, Pan J, Huang S, "A hybrid electrochemical advanced oxidation/microfiltration system using BDD/Ti anode for acid yellow 36 dye wastewater treatment," *Sep. Purif. Technol.*, vol. 120, no. 13, pp. 289–295, Dec. 2013.
- [10] Zhou Y L, Tian R H, Zhi J F, "Amperometric biosensor based on tyrosinase immobilized on a boron-doped diamond electrode," *Biosens. Bioelectron.*, vol. 22, no. 6, pp. 822–828, Jan. 2007.
- [11] Haymond S, Babcock G T, Swain G M, "Direct electrochemistry of cytochrome c at nanocrystalline boron-doped diamond," *J. Am. Chem. Soc.*, vol. 124, no. 36, pp. 10634–10635, Aug. 2002.
- [12] Haubner R, Bohr S, Lux B, "Comparison of P, N and B additions during CVD diamond deposition," *Diamond Relat. Mater.*, vol. 8, no. 2-5, pp. 171–178, Mar. 1999.
- [13] Haubner R, "Comparison of sulfur, boron, nitrogen and phosphorus additions during low-pressure diamond deposition," *Diamond Relat. Mater.*, vol. 14, no. 3-7, pp. 355–363, Mar-Jul. 1999.
- [14] Kalss W, Bohr S, Haubner R, et al, "Influence of boron on diamond growth on WC-Co hardmetals," *Int. J. Refract. Met. Hard Mater.*, vol. 14, no. 1-3, pp. 137–144, Mar. 1996.
- [15] Zhang J G, Wang X C, Shen B, et al. "Effect of boron and silicon doping on improving the cutting performance of CVD diamond coated cutting tools in machining CFRP," *Int. J. Refract. Met. Hard Mater.*, vol. 41, pp. 285-292, Apr. 2013.
- [16] Azevedo A F, Mendes de Barros R C, Serrano S H P, Ferreira N G, "SEM and Raman analysis of boron-doped diamond coating on spherical textured substrates," *Surf. Coat. Technol.*, vol. 200, no. 20-21, pp. 5973–5977, May. 2006.
- [17] Zhao X, Li Y, "Tool Wear Pattern and Mechanics in High Speed Cutting Microwave Printed Circuit Board," *Key Eng. Mater.*, vol. 426-427, pp. 515–519, May. 2010.
- [18] W.M. Zhang, M.H. Hao, Y. Y. Shen, "Ceramic composite materials containing carbon nanotube-infused fiber materials and methods for production," *Mechatronics*, vol. 4, pp. 12–15, Mar. 2004.
- [19] Ager III J W, Walukiewicz W, McCluskey M, et al, "Fano interference of the Raman phonon in heavily boron-doped diamond films grown by chemical vapor deposition," *Appl. Phys. Lett.*, vol. 66, no. 5, pp. 616–618, Nov. 1994.
- [20] May P W, Ludlow W J, Hannaway M, et al, "Raman and conductivity studies of boron-doped microcrystalline diamond, faceted nanocrystalline diamond and cauliflower diamond films," *Diamond Relat. Mater.*, vol. 17, no. 2, pp. 105–117, Feb. 2008.

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