Diamond & Related Materials 63 (2016) 51–59

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Reprint of "A study of CVD diamond deposition on cemented carbide ball-end milling tools with high cobalt content using amorphous ceramic interlayers"☆

Yu-xiao Cui, Wei-song Wang, Bin Shen, Fang-hong Sun *

State Key Laboratory of Mechanical System and Vibration, School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

ARTICLE INFO

Article history:
Received 23 June 2015
Received in revised form 31 July 2015
Accepted 3 September 2015
Available online 6 February 2016

Keywords:
CVD
Diamond films
WC–Co substrates
Interlayer
Adhesion

ABSTRACT

In this paper, CVD diamond coatings are deposited on cemented carbides with 10 wt.% Co using amorphous SiO_2 and amorphous SiC interlayers. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), Raman spectrum and X-ray diffraction (XRD) are carried out to characterize the microstructure and composition of as-deposited films. Moreover, the adhesion and cutting performance of as-fabricated diamond coatings are studied. Indentation tests show that the amorphous ceramic interlayers can enhance the adhesion between diamond films and WC–Co substrates. The cutting tests against zirconia indicate that the tools with amorphous ceramic interlayered diamond coatings exhibit improved cutting performance. The amorphous ceramic interlayers can improve the adhesive strength and wear endurance of diamond coatings on WC–10 wt.% Co substrates, which provide a viable way for adherent diamond coatings on cemented carbide tools with high cobalt content.

1. Introduction

CVD diamond coatings on cemented carbide tools can increase the tool lifetime and cutting performance considerably due to their excellent physical and chemical properties, such as high hardness, low friction coefficient and wear resistance [1–3]. CVD diamond coated tools are very suitable for machining carbon fiber reinforced plastic (CFRP), ceramic, printed circuit board (PCB), metal matrix composite (MMC) and graphite [4–8]. However, the cobalt in cemented carbides can cause graphitization at the film/substrate interface, which can lead to the deterioration of nucleation and growth of CVD diamond. Cobalt removal by chemical etching results in adhesion improvement and is widely used in industry. Nevertheless, the low depth etching will lead to the diffusion of residual cobalt during CVD process, and high depth etching will cause a brittle Co-depleted layer at the interface of film/substrate [9–10]. Either case is detrimental to the adhesion between diamond coatings and WC–Co substrates.

At present, the substrate materials of most diamond coated tools are cemented carbides with low cobalt content, typically in the 3%–6% range [11]. Since higher cobalt content can improve the toughness and strength of cemented carbides, which is extensively used in the intermittent cutting process, well adherent diamond coatings on these cemented carbide tools with high cobalt content is of great importance to the improvement of cutting performance and tool lifetime in difficult-to-cut material machining [12]. To our knowledge, there are a few papers published that investigate the deposition of CVD diamond on the high-cobalt-content cemented carbides by employing either chemical etching [11,13–14] or interlayers [15–17]. Mallika et al. [11] have found that by using chemical etching strong adherent diamond coatings can be deposited on high cobalt cemented carbides. And Xu et al. [10] have obtained adhesion improvement of diamond coatings on cemented carbide with high cobalt content using Nb, Cr and Ta interlayers. According to their study, the specimens performed with both chemical etching and interlayers exhibit better adhesion than those performed with only chemical etching or interlayers. In conclusion, considerable success has been made in obtaining adherent diamond coatings on high-cobalt-content cemented carbides. However, there is little subsequent machining data to verify the effectiveness of as-fabricated diamond coatings.

Amorphous ceramic is in good grace from wide aspects, considering yield strength, break strength, abrasive resistance, corrosion resistance and thermal characteristic [18–19], which makes it very a promising interlayer material. Endler et al. [20] have synthesized a-SiC, a-Si_3N_4 and a-SiC_xN_y interlayers by CVD and performed diamond deposition on those amorphous interlayers. And our former investigations show that a-SiC interlayers can improve the adhesion, frictional behavior and cutting performance of diamond coatings on WC-6 wt.% Co substrates [21–22].

☆ A Publisher's error resulted in this article appearing in the wrong issue. The article is reprinted here for the continuity of the Special Issue: 9th International Conference on New Diamond and New Carbons (NDNC) 2015. For citation purposes, please use the original publication details; Diamond and Related Materials, Volume 59, pp. 21–29.

DOI of original article: http://dx.doi.org/10.1016/j.diamond.2015.09.002.

* Corresponding author.
E-mail address: sunfanghong@sjtu.edu.cn (F. Sun).

http://dx.doi.org/10.1016/j.diamond.2016.01.017
0925-9635/

It has been proved that polycrystalline diamond films can be deposited on SiO_2 with reasonable nucleation rate [23]. Nevertheless, to our knowledge there is few publications to date that describe the application of a-SiO_2 as interlayer material in CVD diamond deposition, which may have pronounced effects on the adhesion of diamond coatings. Therefore, it is necessary to study the influence of a-SiO_2 interlayer on the adhesion of diamond coatings.

Zirconia has a broad range of industrial applications. The excellent properties of zirconia, such as high fracture toughness, chemical resistance, low heat conductivity and good biocompatibility, make it very suitable for producing dental and orthopedic implants in medical field. Nevertheless, such ceramics are not easy to be manufactured due to the abrasive character of ceramic debris during machining. CVD diamond coated tools are very promising in machining abrasive materials. And yet there is very few data available insofar as zirconia is concerned as test medium [6]. In this paper, by the combination of amorphous ceramic interlayers and chemical etching, CVD diamond coatings with improved adhesion have been fabricated on WC-10 wt.% Co substrates. In particular, the amorphous ceramic interlayered diamond coatings are deposited on cemented carbide ball-end milling tools (Co 10 wt.%). The effectiveness of amorphous ceramic interlayers has been validated by milling zirconia ceramic.

2. Experimental

The cemented carbide samples with 10 wt.% Co are used as substrates. A two-step chemical pretreatment is performed in prior to remove surface cobalt and roughen the substrate as well, which is reported elsewhere [21]. The WC–Co substrates are dipped in the Murakami's regent ($10\ g\ K_3[Fe(CN)]_6 + 10\ g\ KOH + 100\ ml\ H_2O$) in ultrasonic vessel for 15 min; then the surface binder phase was washed away in the acid ($30\ ml\ H_2SO_4 + 70\ ml\ H_2O_2$) for 1 min. Subsequently the amorphous ceramic interlayers are synthesized in a home-made CVD apparatus, with tetraethoxysilane (TEOS) and dimethyldiethoxysilane (DMDEOS) as the precursors of a-SiO_2 and a-SiC respectively. After the fabrication of amorphous ceramic interlayers, as-pretreated WC–Co substrates are scratched with 3 μm diamond powder and cleaned in ultrasonic deionized water bath to enhance diamond nucleation prior to diamond deposition. Then CVD diamond coatings are deposited with acetone and hydrogen as reactant. The deposition parameters of interlayers and CVD diamond are given in Table 1. Table 2 gives the different deposition processing conditions in this study. In particular, conventional WC–Co substrates with lower Co content (Sample 2 and Sample 6) are also employed in this work, which are prepared using the same pretreatment and deposition process.

The interlayer material (a-SiO_2 and a-SiC) is investigated by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) to study the microstructure and phase composition. The interlayer material is mixed with alcohol, and it is ground into sub-microscale regimes in a mortar and pestle. Subsequently, the turbid liquid with ground interlayer material is placed in ultrasonic vessel for 15 min to be well mixed. After that 50 μl of the turbid liquid is dropped onto carbon film, which is mounted on copper grid as support. The carbon film with turbid liquid is dried under a lamp for 30 min. Then the carbon film is placed in the vacuum cavity and the microstructure of grinded interlayer material is detected by TEM.

Table 1
Deposition parameters of interlayers and diamond coatings.

Parameters	a-SiO_2 and a-SiC	Diamond	
		Nucleation	Growth
Pressure	12 Torr	15 Torr	30 Torr
Gas flow	100 sccm	300 sccm	300 sccm
Precursor source/H_2 ratio	0.5%	–	–
Acetone/H_2 ratio	–	1%	1%
Filament-substrate distance	15 mm	10 mm	10 mm
Filament temperature	2200 °C	2200 °C	2200 °C
Substrate temperature	700 °C	800 °C	800 °C
Negative bias current	–	4 A	4 A

Table 2
List of different deposition processes for WC–Co cemented carbide substrates.

Sample	Chemical etching	Interlayer	Co content	Diamond deposition
1	Yes	–	10 wt.%	–
2	Yes	–	6 wt.%	–
3	Yes	a-SiO_2 (40 min)	10 wt.%	–
4	Yes	a-SiC (30 min)	10 wt.%	–
5	Yes	–	10 wt.%	4 h
6	Yes	–	6 wt.%	4 h
7	Yes	a-SiO2 (40 min)	10 wt.%	4 h
8	Yes	a-SiC (30 min)	10 wt.%	4 h

Field emission gun scanning electron microscopy (FEG-SEM) is used to investigate the morphologies of amorphous ceramic intermediate films and CVD diamond films. Energy dispersive X-ray spectroscopy (EDX) measurements are used to give an elemental analysis of the a-SiO_2 interlayer coated substrates and conventional chemical etched substrates. The quality and crystalline microstructure of as-synthesized diamond coatings are analyzed by Raman spectroscopy and X-ray diffraction (XRD). In order to evaluate the adhesive strength between diamond coatings and WC–Co substrates, Rockwell indentation tests are performed on as-synthesized diamond coatings, with a constant load of 100 kg. The indentation on each specimen is investigated by SEM respectively.

To analyze the cutting performance of as-fabricated diamond coated tools, comparative milling tests are conducted for diamond coated tools with/without amorphous interlayers, with zirconia ceramic as the work piece. The details of zirconia ceramic are given in Table 3. The milling parameters are as follows: spindle speed, 8000 rpm; feed rate, 0.3 mm/rev, radial cutting width, 0.3 mm; cutting depth, 0.5 mm. No lubricants are used in the cutting test. The worn morphology of cutting edge and the flank wear values are investigated by optical microscope and SEM respectively.

3. Results and discussion

The amorphous ceramic interlayers (a-SiO_2 and a-SiC) are synthesized by pyrolysis of molecular precursors. In order to investigate the microstructure and phase composition of interlayer material, TEM analysis is applied. After sufficiently mechanical crushing, the interlayer material is grinded into sub-microscale regimes. As shown in Fig. 1a–b, the dark particles of a-SiO_2 and a-SiC can be observed, with sizes between 100 and 200 nm. For both types of interlayer materials, the SAED patterns of sub-microscale regimes consist of only broad and dull halos, indicating the presence of amorphous structure.

The SEM micrographs and EDX patterns of amorphous ceramic interlayers and chemical etched WC–Co substrates (Samples 1–4) are shown in Fig. 2 by SEM. It can be seen from Fig. 2a and c that after chemical etching the surface topography of Samples 1–2 is quite alike. The cobalt on cemented carbide substrate surface is washed away and the WC grains present a rough and porous Co-depleted layer. When amorphous ceramic interlayers are employed, as shown in Fig. 2e and g, homogeneous pasty-like materials, i. e. a-SiO_2 and a-SiC, are covered on the rugged WC grains, and the surface topography is close in texture with ball-like

Table 3
Properties of zirconia ceramic.

Density (g/cm^3)	6.03
Mean grain size (μm)	0.4
Young's modulus (GPa)	222
Fracture Toughness ($Pam^{1/2}$)	10.7 ± 0.7
Hardness (kg/mm^2)	1180 ± 13