Growth of diamond coatings on functionally graded cemented carbides

Yong Liu [a,*], Meng Du [a], Mingyang Zhang [a], Qiuping Wei [b], Zhiming Yu [b], Xiaofeng Li [a]

[a] *State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, PR China*
[b] *School of Materials Science and Engineering, Central South University, Changsha 410083, PR China*

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ABSTRACT

Cemented carbides with diamond coatings have been widely used for cutting tools. However, the reaction of Co with the diamond coating during the deposition leads to the deterioration of the coating structure and the bonding strength. In this work, functionally graded cemented carbides (FGCCs), with a WC-rich surface, Co-rich intermediate layer and η phase-containing central part, were prepared. Diamond coatings were prepared on the FGCC by the hot filament chemical vapor deposition (HFCVD), a method of catalytic decomposition of methane and hydrogen mixtures at a heated filament. The crystal growth and the bonding behavior of diamonds to different layers in FGCCs were investigated. Results indicated that the different regions of FGCCs show apparently different grain sizes and morphologies of diamond coatings. The Co-poor layer has a high crystallinity and purity of diamond, and the η phase-containing region is beneficial for the formation of fine diamond grains. The Co-rich layer has a diamond coating of low bonding strength due to the formation of graphite and porosity, while the η phase-containing region has a high bonding strength. By the combined effects of the three different layers, FGCC shows generally a high bonding strength, and is promising for using as a substrate for the diamond coating.

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1. Introduction

With the progress of modern machinery industries, the cutting efficiency has been increased very quickly. Under many conditions, high speed, high precision and very wear-resistant cutting tools are required. WC–Co cemented carbides are one of the mostly used cutting tools for steels and other conventional materials due to their high hardness, reasonable toughness and lifetime. However, cemented carbides cannot be effectively applied in cutting aluminium-based composites, ceramics, titanium and carbon fiber-reinforced composites [1,2]. In the above cases, the high reactivity of Co to the cutting metals and the insufficient hardness of cemented carbides fail to meet the requirements for high-speed and long-life cutting [3].

One of the developments of the next generation of cemented carbides is the coating of diamond films. Diamond is the hardest material in natural environment, with such advantages as high heat conductivity, low friction coefficient and excellent chemical stability to most materials. The wear resistance of cemented carbides with diamond coatings is significantly improved, and the lifetime can be prolonged as long as 5–10 times compared with conventional cemented carbides [4,5]. Moreover, the surface roughness of the machined parts is obviously enhanced. There are many successful methods for coating diamonds on cemented carbides, including HFCVD [6,7], microwave chemical vapor deposition [8], and flame deposition [9].

The main obstacle for the applications of diamond coatings is the poor bonding strength to the cemented carbide substrates. There are both physical and chemical misfits between the diamond coatings and the cemented carbides. The thermal expansion coefficient of cemented carbides is much higher than that of the diamond, so cracks may form during the cooling and subsequent cutting process [10]. There is no chemical bonding between cemented carbides and the diamond coatings, and the Co phase in cemented carbides will promote the formation of graphite during the chemical vapor deposition, instead of the diamond phase [11,12]. The existence of impurity phases, such as graphite and amorphous carbon, is detrimental for the hardness of the diamond coating and its bonding to the substrate [13]. Therefore, avoiding the contact of the Co phase to the diamond is of significant importance for increasing the bonding strength. For the depletion of Co phase, cemented carbides are usually etched by using Murakami solution at first, in order to remove the boundaries of WC grains in the surface, and then, the samples are etched by using acid for the elimination of Co [14]. Another way is to introduce intermediate layers, for example, Si [15], W [16], B [17] and Cr [18], such that the diamond can grow without the influence of Co phase. However, the depletion of Co will leave porosity behind, and the introduction of intermediate layers will bring about some unnecessary phases.

There are other ways to remove or decrease Co phase from the surface of cemented carbides. In 1980s, Sandvick developed the first functionally graded cemented carbide with WC–Co compositions, which

* Corresponding author at: State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, Hunan, PR China.
E-mail address: yonliu@csu.edu.cn (Y. Liu).

Table 1

HFCVD parameters for deposition of diamond coatings on FGCC.

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Filament temperature/°C	2000
Deposition distance/mm	9 ± 1
Substrate temperature/°C	700
Gas pressure/Torr	30 ± 1
CH_4/H_2 (vol.%)	3
Deposition time/min	300
Cooling time/min	180

had a WC-rich surface, Co-rich intermediate layer and conventionally central region [19]. The sandwich-like structure can be clearly seen by naked eyes. In 1990s, there was another graded structure for WC–TiC–Co cemented carbides, on which either Co-rich or Co-poor layer can be formed [20]. In this case, the graded structure is much thinner, and usually in a scale of tens of microns. There are some reports on coating diamond on the latter graded structure, but no study on the former one is conducted. This work aims to study coating diamond on the sandwich-like graded structure, and investigate the influence of the graded microstructures on the growth and the bonding behavior of diamonds.

2. Experimental

The functionally graded cemented carbides were prepared via the carburization of carbon-deficient or η phase-containing pre-sintered WC–6Co (wt.%) specimens. The preparation process was described by the authors in Ref. [21] in detail. The FGCC specimens were cut in the cross section, grounded first with emery paper, and then polished by using diamond disks embedded with diamonds of different sizes, then a two-stepped etching method was conducted: (1) etching by using Murakami's reagent (10 g $K_3[Fe(CN)_6]$ + 10 g K OH + 100 ml H_2O) for 3 min in an ultrasonic vessel to rough the WC surface; (2) etching in an acidic solution of hydrogen peroxide (2 ml 96 wt.% H_2SO_4 + 2 ml 68 wt.% HNO_3 + 20 ml 40% H_2O_2 + 40 ml H_2O) for 3 min in order to remove Co phase in the surface. The as-etched specimens were then abraded ultrasonically in a suspension of diamond powder in a size of sub-micron (<500 nm) in acetone for 30 min. This treatment encourages the subsequent inhomogeneous nucleation of diamond during the chemical vapor deposition, by implanting ultrafine diamond fragments into the substrate surface, and by creating suitable surface defects. The diamond coatings were prepared by using a HFCVD. The deposition parameters are shown in Table 1.

Scanning electron microscopy (Quanta FEG 250 Environmental SEM) was used to observe the surface morphologies of the substrates and the diamond coatings. Energy dispersive X-ray spectroscopy was utilized to analyze the chemical compositions in the surface. The quality of the diamond coatings was assessed by Raman spectroscopy (Lab RAM Aramis) at an excitation wavelength of 532 nm. Scratch tests were used to quantitatively determine the bonding strength of the diamond coatings to WC–Co substrates. The scratch tests were carried out by using Multi-Specimen Test System from CETR Instruments (Model UMT-3), equipped with a Rockwell C diamond cone indenter. The included angle of the diamond cone is 120°, and the radius of the hemispherical tip is 200 μm. A scratch length of 9 mm was used with a progressively normal loading of 1 to 50 N. During the scratch test, the values of the
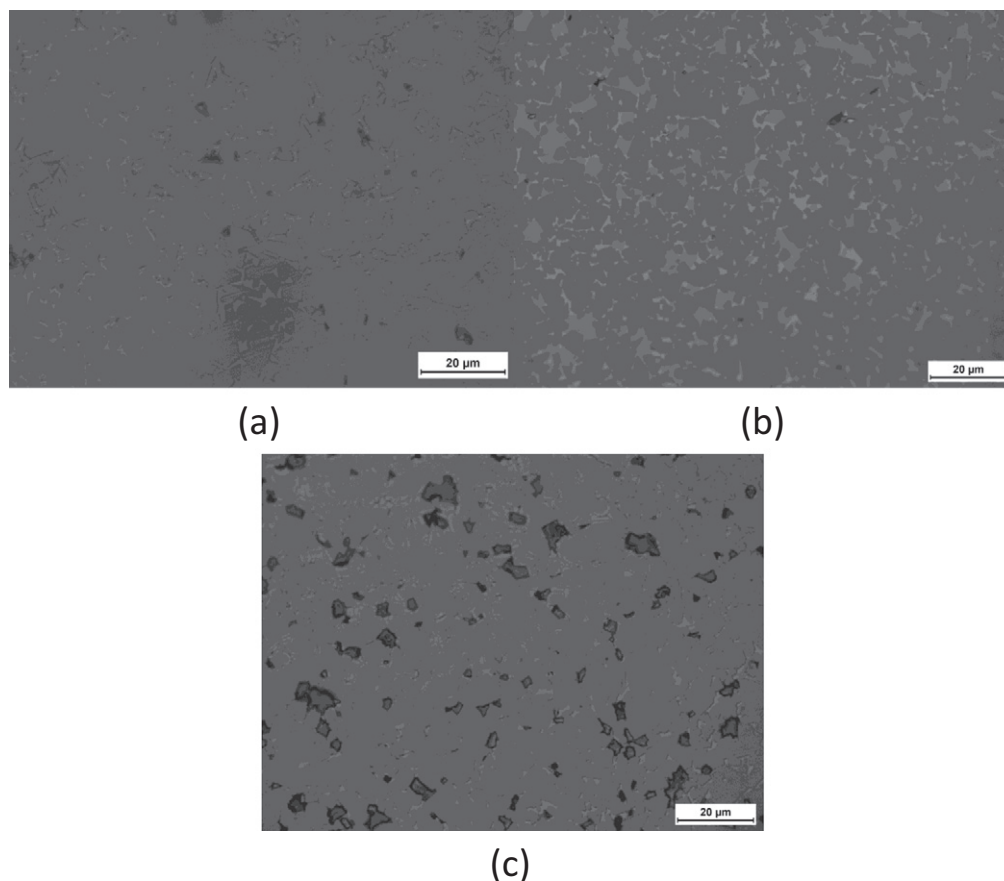
Fig. 1. Microstructures of FGCC: (a) surface with a coarse WC and Co-poor structure; (b) intermediate layer with Co-rich structure; (c) center part with WC + Co + η structure.
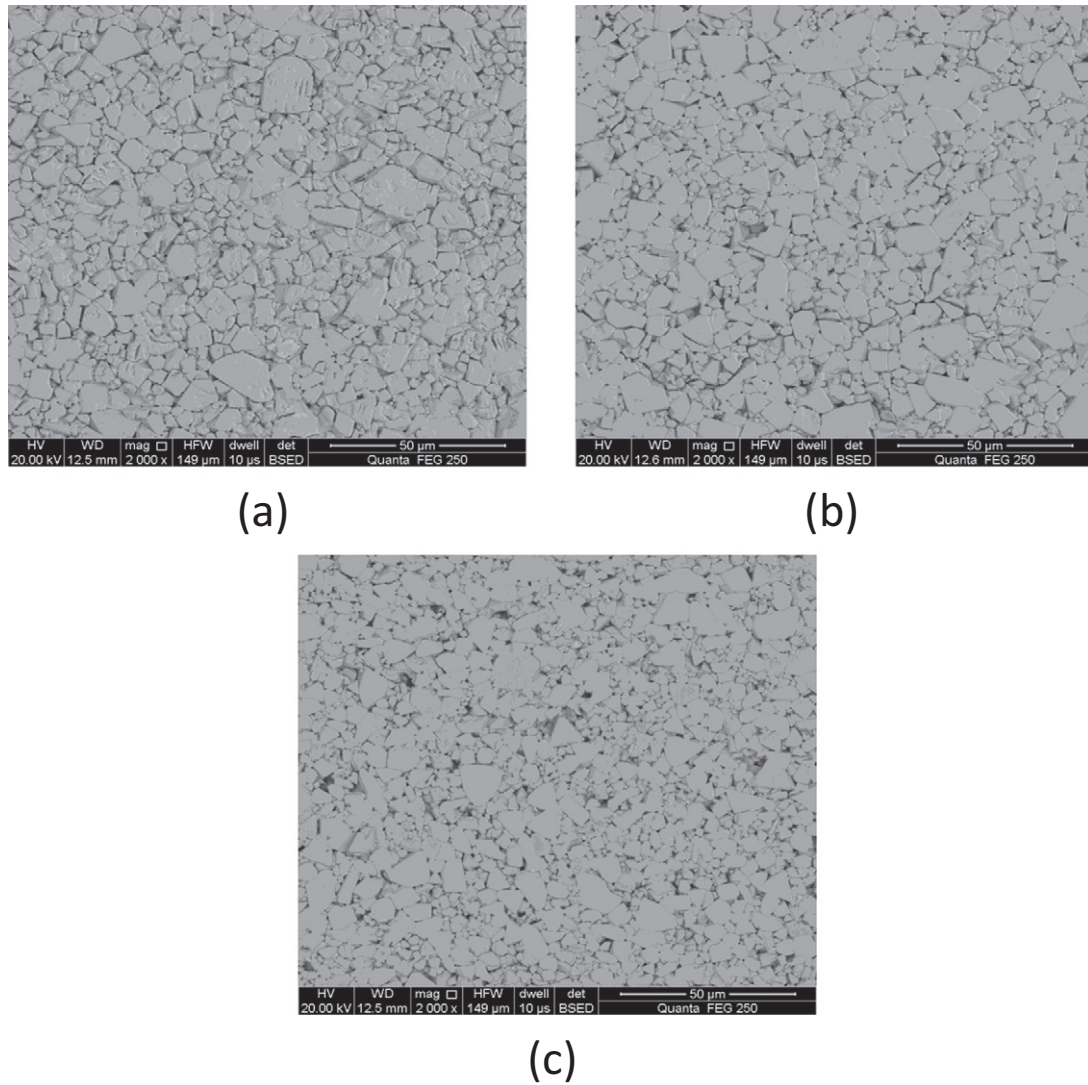
(a)

(b)

(c)

Fig. 2. Etched microstructures of FGCC: (a) rounded WC grains in surface layer; (b) depletion of Co in the mid layer; (c) remaining of η phase in center part.

tangential and the normal force were acquired. For measuring the adhesive failure of the diamond coating with the substrate, 12 scratching tests were performed on 4 specimens.

3. Results

In this work, a FGCC with coarse-grained WC was used. Fig. 1 shows the microstructures in different regions. The surface layer is rich in WC, with a grain size of about 6.5 μm and a content of Co about 3–4 wt.%. The center part consists of WC, Co and η phase (the gray phase), and has a Co content about 5.8 wt.%, as shown in Fig. 1(c). In between the surface and the center part, there is an intermediate Co-rich layer with a content of Co about 8 wt.% (Fig. 1(b)). After two-stepped etching, the WC grains in the surface layer are obviously rounded and roughened, and most Co phase in between WC grains is eliminated (Fig. 2(a)). In Co-rich layer, porosities can be seen after the Co phase is removed (Fig. 2(b)), while the WC grains still have a truncated shape. Porosities also exist in the center part where most of η phase is eliminated (Fig. 2(c)). Therefore, the etching behavior of different layers in FGCC is different, and the remaining microstructure is also different.

Fig. 3 shows the diamond grains growing on different surfaces of FGCC. The diamonds are equiaxed and well-crystallized, but are different in size in different regions. The mean grain sizes of diamonds on

the surface, Co-rich and the center part are 3.2, 2.8 and 2.4 μm, respectively. The cross sections of diamond coatings show a column-structured grain growth behavior. The coatings are rather uniform, and seem to be closely bonded with the FGCC (Fig. 4). Quantitative measurements show that there is a difference in the thickness of diamond coatings in different regions. From the surface to the center part, the thickness of coatings drops a little, as shown in Fig. 4(d). Raman spectroscopy analyses of the cross-section in Fig. 5 indicate that the diamonds have a sharp peak and are well-crystallized, but in the Co-rich layer, the graphite phase exists obviously.

For measuring the bonding strength of the diamond coating to the substrate, the specimens were scratched by using a diamond cone under a pressure of 50 N. Scratching tests were performed separately in different regions. On both the outer layer and the Co-rich layer, the diamond coatings are broken (Fig. 6(a) and (b)), but on the center part the diamond coating is almost intact (Fig. 6(c)). Moreover, the edge of the broken coating on the Co-rich layer is zigzagged, indicating that the secondary cracking occurred during the scratching. The total delamination area is very large on the coating of the Co-rich layer, which indicates a poor adhesion. The bonding strength also depends on the strength of the diamond coatings, and the secondary cracking on the Co-rich layer indicates a poor strength of the diamond coating. Fig. 7 shows the increase of the tangential force with the applied normal
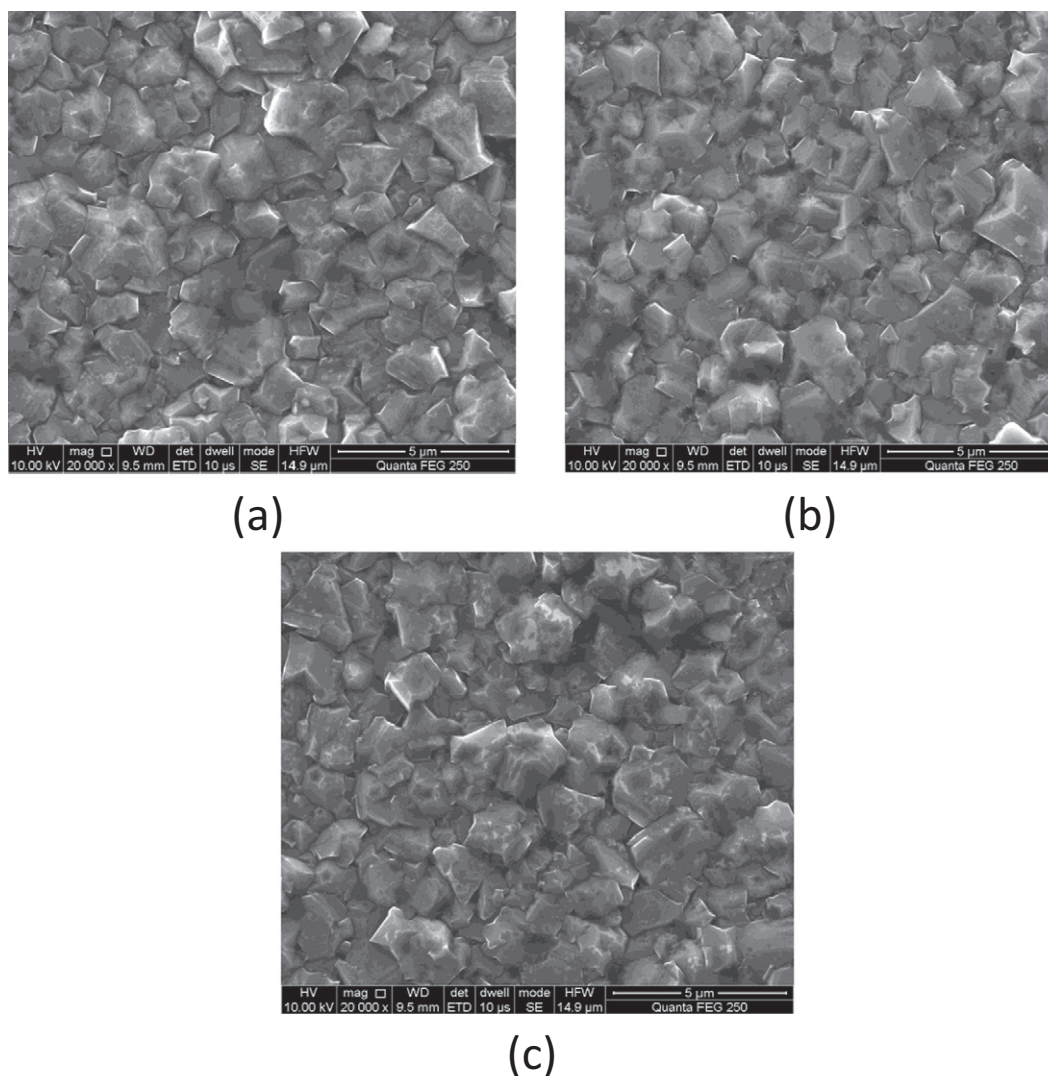
(a)

(b)

(c)

Fig. 3. Diamond crystals grew on different regions of FGCC: (a) WC-rich layer; (b) Co-rich layer; (c) center part.

load. It indicates that the tangential force increases linearly first, followed by considerable fluctuations. Generally, the tangential force increases abruptly due to the release of elastic energy when the failure of the coating occurs. And the normal load at which the failure occurs is defined as the critical load. For scratch 2 (Co-rich layer), the tangential force changes rapidly around a normal force of 31 N, but the rapid changing of tangential force of scratch 3(WC-rich layer) is not obvious. The tangential force of scratch 1(Center part) keeps a linear relation with the normal force. To identify the exact critical load and the delamination for each scratch, it is more reliable to combine the onset of the change of the tangential force with the microscopic observation [22]. It is found that the scratches 2 and 3 on the coatings fail at a distance of about 5.58 and 7.02 mm, respectively, corresponding well to the change of loads at 31 N and 39 N in Fig. 7. Since there is no indication of sudden change of the tangential force in the center part, and no delamination is found in Fig. 6(c), the coating has the highest bonding strength. Fig. 8 shows the delaminated surfaces of different regions. In the Co-rich region, there is obvious micro-cracking of diamonds occurred in between WC grains (Fig. 8(a)). The diamond grains in the original sites of the Co phase are not well crystallized, and scraps of small particles can be seen on the WC grains, as shown in Fig. 8(c). The surface of the broken outer layer is much cleaner (Fig. 8(b)), and diamond grains can be seen to grow closely in the sites where the original Co phase was (Fig. 8(d)).

4. Discussions

The growth of diamonds strongly depends on the chemistry and the morphology of the cemented carbide substrate. The main factors are the content of Co and the surface roughness. For the area originally with a high Co content about 8 wt.%, during the process of HFCVD at 700 °C, Co could diffuse to the surface and dissolve carbon at high temperatures, leading to the formation of graphite, amorphous carbon and other impurities [13]. Even with a rougher surface than the WC-rich region, the Co-rich region does not show a higher adhesive strength due to improved mechanical interlocking, because the porosity in the surface acts as a channel for the diffusion of Co. Thus, it is difficult to grow diamonds on cemented carbides of high contents of Co. The FGCC has varied distributions of Co in different regions. In the Co-rich region, even after two-stepped etching, the deteriorative effect of Co phase cannot be completely eliminated. The surface layer is poor in Co, and the center part contains η phase which also consumes a part of Co phase, so the effect of Co phase can be effectively decreased. The center region also has a higher surface roughness than the WC-rich region, but shows a higher bonding strength between the coating and the substrate due to the decrease of Co phase.

The bonding strength of diamond coating to the cemented carbide substrate is significantly degraded by the graphite phase [15]. The
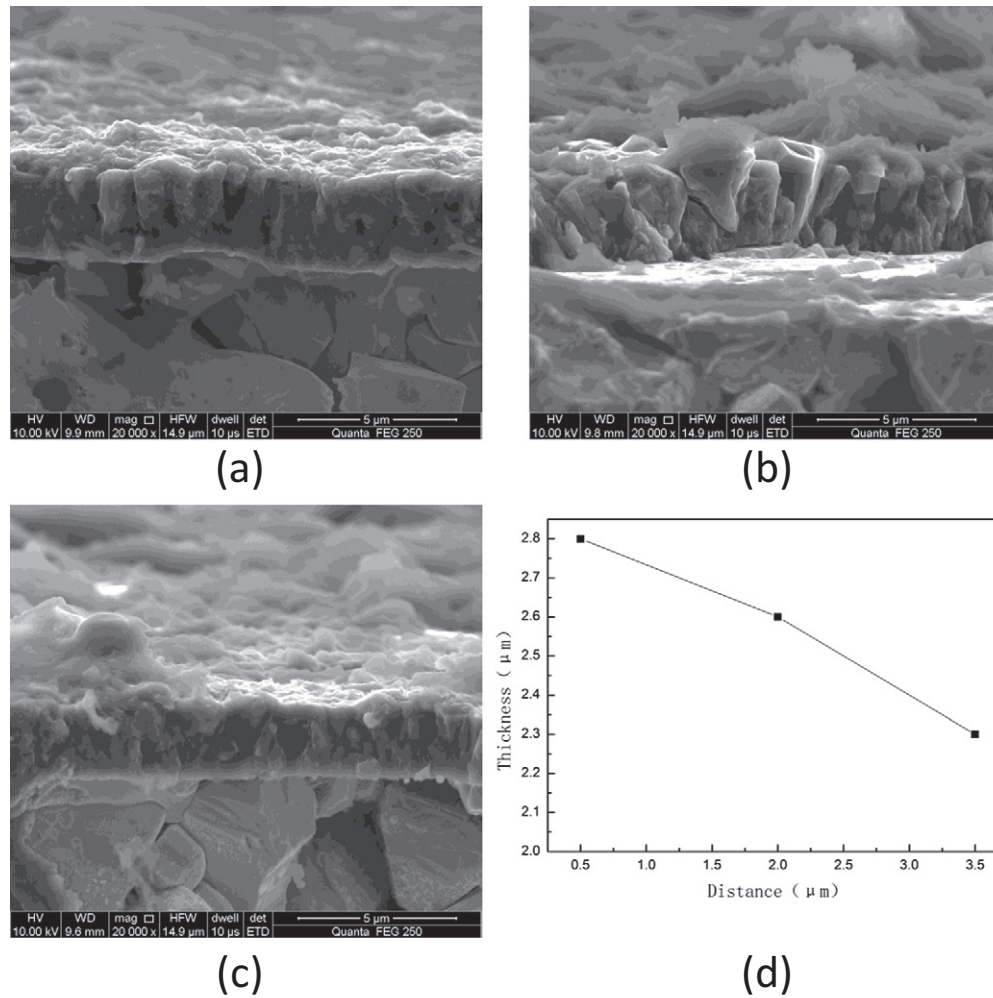
Fig. 4. Cross sections of diamond coatings grew on different regions of FGCC: (a) WC-rich layer; (b) Co-rich layer; (c) center part; (d) thickness.

graphite phase in Co-rich layer decreases the crystallinity of diamonds, and induces micro-cracks during both the deposition and the loading process. Since the surface layer is poor in Co, the bonding strength of diamond coating is higher than that on the Co-rich layer. It is interesting that the η phase-containing center part has the highest bonding strength.
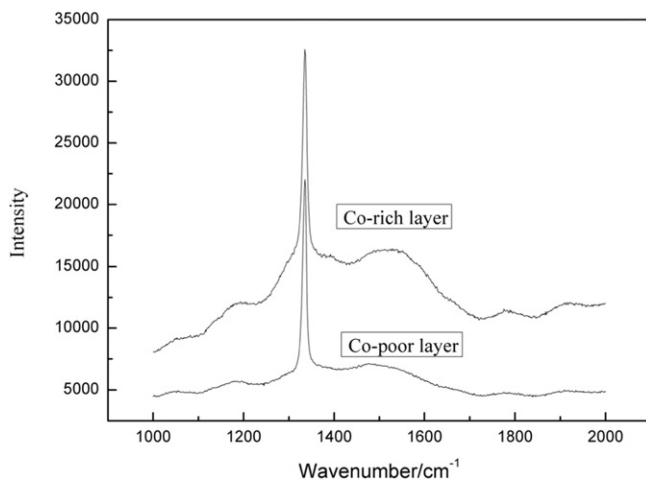

Fig. 5. Raman spectra of the diamond coating on (a) Co-rich layer showing existence of graphite; (b) Co-poor layer with pure and well-crystallized diamond phase.

It may be due to the fact that the content of Co phase is lower than that in other areas. During the deposition process, less Co diffuses to the surface, so the diamond coating on the center part is more crystalline. Moreover, η phase itself can promote the nucleation of diamonds. The fact that the average size of diamond grains is the smallest on the center region (Fig. 3(c)) also implies the highest bonding strength and the coating strength. Usually, η phase-containing cemented carbides should be avoided for their high brittleness. However, it seems that this kind of structure may be useful for coating diamonds.

Considering the fact that the thickness of the diamond coating on FGCC is rather thin, the bonding strength is basically very high. The reason may be due to the coarse grain size of WC and the graded structure. After the etching, the coarse WC may provide continuous and rough surface for the growth of diamonds. The Co-rich layer in FGCC may release the thermal stress during the deposition, and prevent the formation of cracks in other regions. Although, the η phase-containing cemented carbide cannot be used separately, it can provide a high bonding strength to diamond coatings. All these beneficial effects combine together, making FGCC a promising substrate for coating polycrystalline diamonds.

5. Conclusions

[1] The different regions of FGCC, containing varied Co-concentrations, WC grain sizes and phase compositions, show apparently different morphologies of diamond coatings. The Co-poor layer has a high crystallinity and purity of
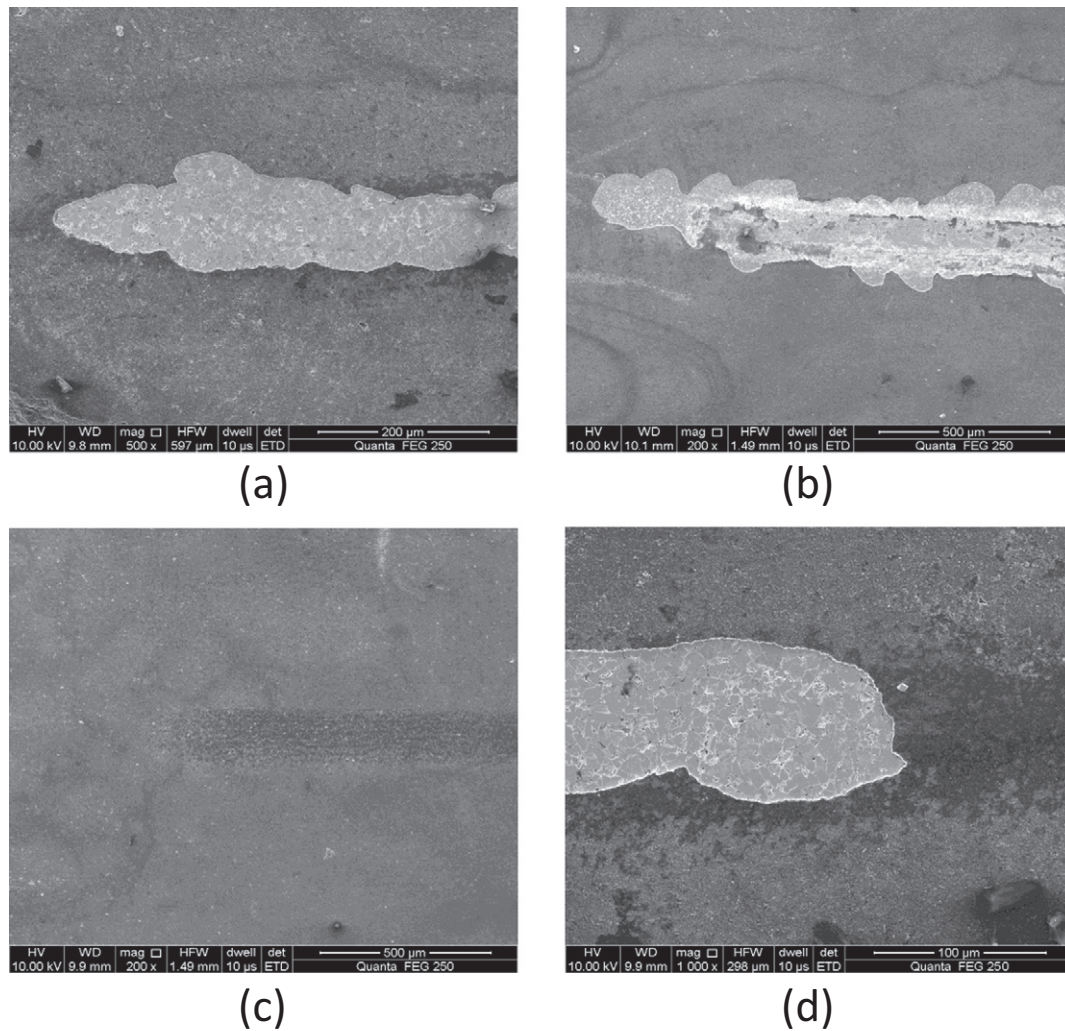
Fig. 6. Scratches on diamond coatings above different regions of FGCC: (a) WC-rich layer; (b) Co-Rich layer; (c) Center part.

diamond, and η phase-containing region is beneficial for the formation of fine diamond grains.

[2] The Co-rich layer has a diamond coating of a low bonding strength due to the formation of graphite and porosity on the interface, while the η phase-containing region has a high bonding strength.

[3] By the combined effects of the three different layers, FGCC shows generally a high bonding strength to the diamond coating.
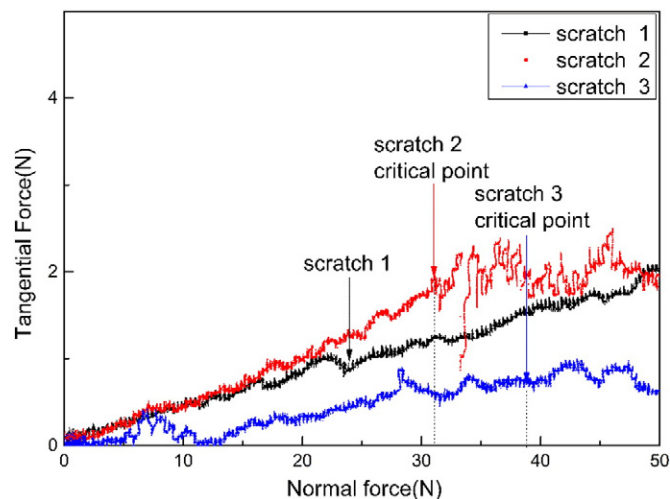

Fig. 7. Scratching behaviors of the diamond coatings in different regions of FGCC (scratches 1, 2 and 3 correspond to (c), (a) and (b) in Fig. 6).

References

[1] R. Polini, F. Casadei, P. D'Antonio, E. Traversa, Dry turning of alumina/aluminum composites with CVD diamond coated Co-cemented tungsten carbide tools, Surf. Coat. Technol. 166 (2003) 127–134.
[2] H. Gomez, D. Durham, X. Xiao, M. Lukitsch, P. Lu, K. Chou, et al., Adhesion analysis and dry machining performance of CVD diamond coatings deposited on surface modified WC–Co turning inserts, J. Mater. Process. Technol. 212 (2012) 523–533.
[3] H. Saito, A. Iwabuchi, T. Shimizu, Effects of Co content and WC grain size on wear of WC cemented carbide, Wear 261 (2006) 126–132.
[4] Z.M. Zhang, H.S. Shen, F.H. Sun, X.C. He, Y.Z. Wan, Fabrication and application of chemical vapor deposition diamond-coated drawing dies, Diamond Relat. Mater. 10 (2001) 33–38.
[5] K. Kanda, S. Takehana, S. Yoshida, R. Watanabe, S. Takano, H. Ando, et al., Application of diamond-coated cutting tools, Surf. Coat. Technol. 73 (1995) 115–120.
[6] S.K. Sarangi, A. Chattopadhyay, A.K. Chattopadhyay, Effect of pretreatment methods and chamber pressure on morphology, quality and adhesion of HFCVD diamond coating on cemented carbide inserts, Appl. Surf. Sci. 254 (2008) 3721–3733.
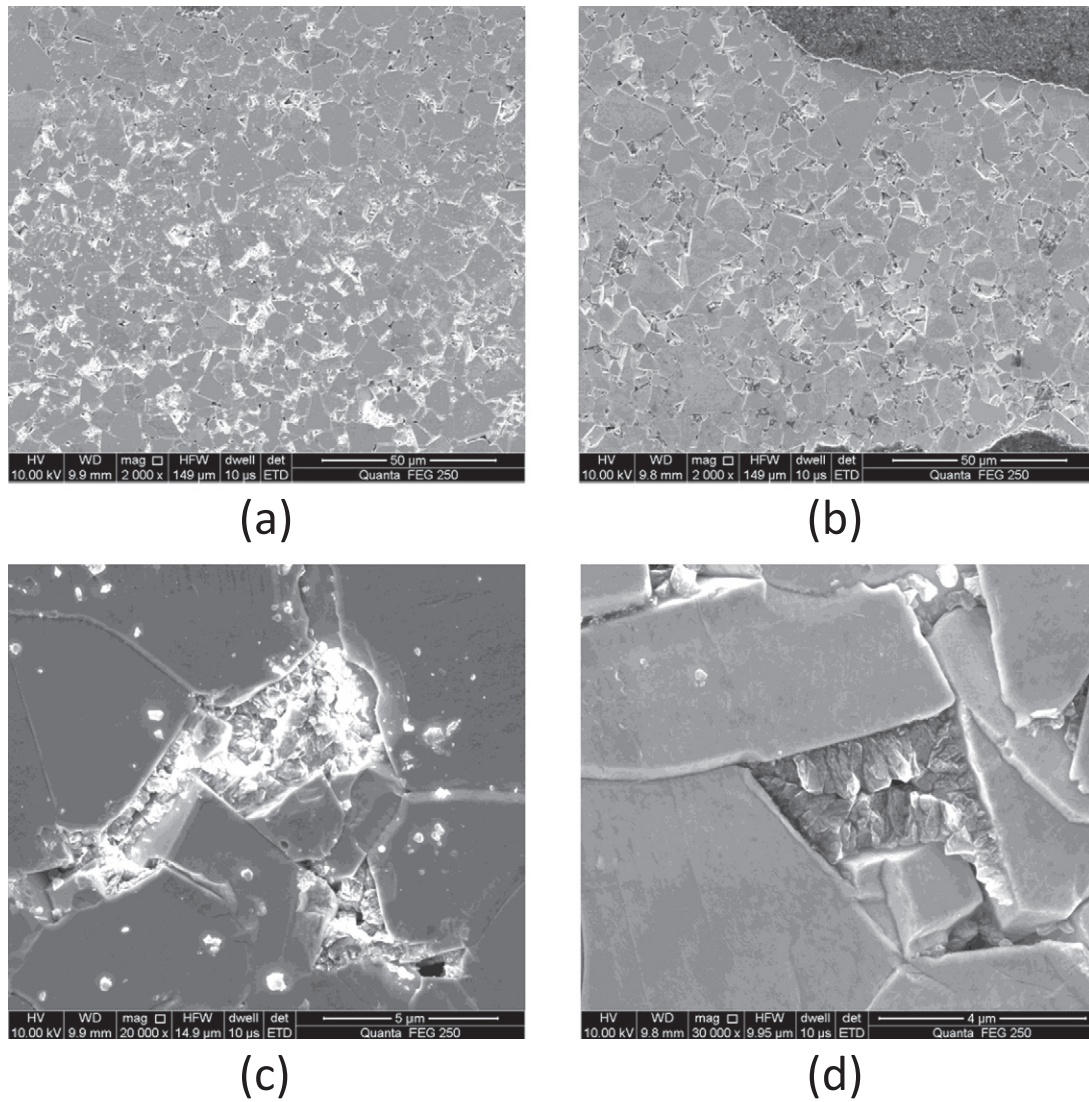
Fig. 8. Microstructures of the broken surface of the diamond coatings on (a) Co-rich layer; (b) WC-rich layer; and magnifications of diamond growth in Co-rich layer (c) and WC-rich layer (d).

[7] H. Sein, W. Ahmed, M. Jackson, R. Polini, I. Hassan, M. Amar, et al., Enhancing nucleation density and adhesion of polycrystalline diamond films deposited by HFCVD using surface treatments on Co cemented tungsten carbide, Diamond Relat. Mater. 13 (2004) 610–615.

[8] K. Mallika, R. Komanduri, Diamond coatings on cemented tungsten carbide tools by low-pressure microwave CVD, Wear 224 (1999) 245–266.

[9] S. Marinković, S. Stanković, Z. Rakočević, Effects of cemented carbide surface pre-treatment in combustion flame chemical vapour deposition of diamond, Thin Solid Films 354 (1999) 118–128.

[10] D. Jianxin, Z. Hui, W. Ze, L. Aihua, Friction and wear behavior of polycrystalline diamond at temperatures up to 700 °C, Int. J. Refract. Met. Hard Mater. 29 (2011) 631–638.

[11] A.K. Mehlmann, S. Berger, A. Fayer, S.F. Dirnfeld, M. Bamberger, Y. Avigal, et al., Investigation of cobalt behaviour during diamond deposition on cemented carbides, Diamond Relat. Mater. 3 (1994) 805–809.

[12] W. Tang, Q. Wang, S. Wang, F. Lu, Adherent diamond coatings on cemented carbide substrates with different cobalt contents, Diamond Relat. Mater. 10 (2001) 1700–1704.

[13] F.H. Sun, Z.M. Zhang, M. Chen, H.S. Shen, Improvement of adhesive strength and surface roughness of diamond films on Co-cemented tungsten carbide tools, Diamond Relat. Mater. 12 (2003) 711–718.

[14] Q. Wei, M.N.R. Ashfold, Y.A. Mankelevich, Z.M. Yu, P.Z. Liu, L. Ma, Diamond growth on WC–Co substrates by hot filament chemical vapor deposition: effect of filament–substrate separation, Diamond Relat. Mater. 20 (2011) 641–650.

[15] F. Fan, W. Tang, S. Liu, L. Hei, C. Li, G. Chen, et al., An effort to enhance adhesion of diamond coatings to cemented carbide substrates by introducing Si onto the interface, Surf. Coat. Technol. 200 (2006) 6727–6732.

[16] K. Vandierendonck, C. Quaeyhaegens, M. Nesladek, J. D'Haen, J. Vlekken, M. D'Olieslaeger, et al., Study of the diamond deposition on cemented carbides containing 10 wt.% Co with a tungsten intermediate layer, Surf. Coat. Technol. 74–75 (1995) 819–826.

[17] W. Tang, Q. Wang, S. Wang, F. Lu, A comparison in performance of diamond coated cemented carbide cutting tools with and without a boride interlayer, Surf. Coat. Technol. 153 (2002) 298–303.

[18] R. Polini, M. Barletta, G. Cristofanilli, Wear resistance of nano- and micro-crystalline diamond coatings onto WC–Co with Cr/CrN interlayers, Thin Solid Films 519 (2010) 1629–1635.

[19] A.F. Lisovsky, On the imbibition of metal melts by sintered carbides, Powder Metall. Int. 19 (1987) 18.

[20] W. Lengauer, K. Dreyer, Functionally graded hardmetals, J. Alloys Compd. 338 (2002) 194–212.

[21] Y. Liu, H. Wang, Z. Long, P.K. Liaw, J. Yang, B. Huang, Microstructural evolution and mechanical behaviors of graded cemented carbides, Mater. Sci. Eng. A 426 (2006) 346–354.

[22] A.J. Perry, Scratch adhesion testing of hard coatings, Thin Solid Films 107 (1983) 167–180.