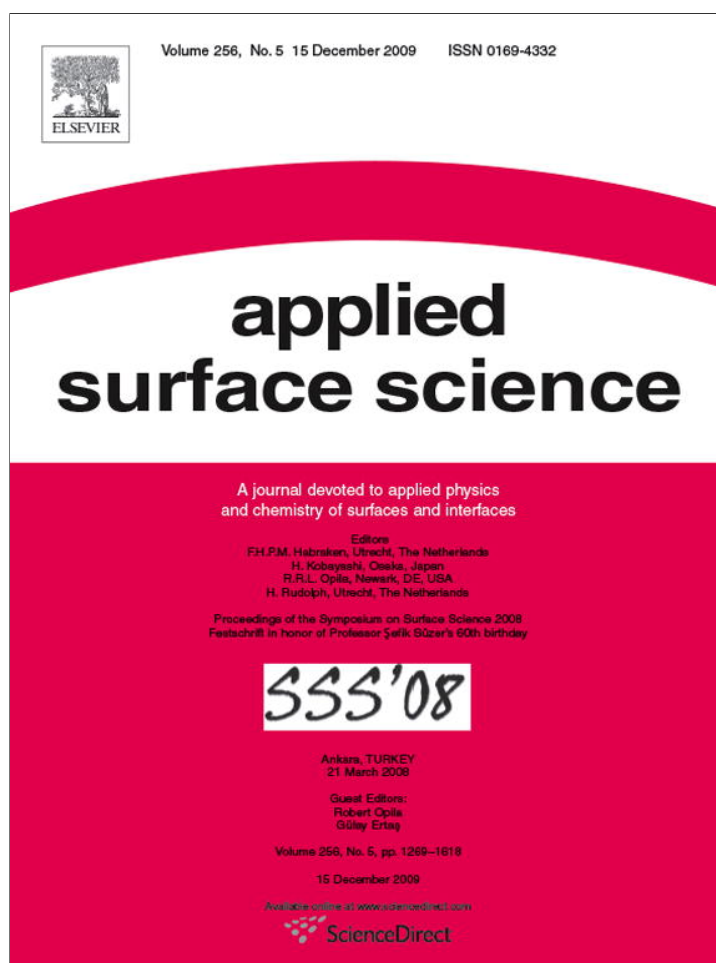




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The effects of temperature on nanocrystalline diamond films deposited on WC–13 wt.% Co substrate with W–C gradient layer

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ABSTRACT

A tungsten-carbide gradient coating (WCGC) was prepared by reactive sputtering as an intermediate layer on the cemented carbide, WC–13 wt.% Co, substrate to improve the nucleation, smoothness and adhesion of diamond film. The diamond film was deposited by hot filament chemical vapor deposition (HFCVD). The effects of the substrate temperature on the WCGC and the diamond film were investigated. The characterization of the WCGC and the diamond films was analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), micro-Raman spectroscopy and Rockwell hardness indentation. It is found that the WCGC plays an important role in improving the nucleation, smoothness and adhesion of diamond film; and the diamond films exhibit better quality and adhesion as substrate temperature increases during the CVD processes.

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1. Introduction

At present, the materials of cutting tools, sliding bearings, drawing dies and many kinds of wear resistant components are mostly cemented carbide [1]. In order to prolong the lifetime of these tools, coatings of super-hard materials are often applied [2–4]. Due to its super-high hardness, low friction, low thermal expansion coefficient, high thermal conductivity and good chemical stability, diamond film is widely used as hard coating to cemented carbide tools for machining non-ferrous metals and alloys, wood, chip-board and hard brittle non-metals (e.g., ceramics, graphite, reinforced plastics) [5–7].

However, direct deposition of diamond on the cemented carbide is difficult because of the presence of the Co binder phase. The cobalt promotes the formation of a non-diamond phase, resulting in very poor adhesion [8,9]. In order to suppress the negative effect of cobalt, many pretreatment methods such as selective etching of Co [10–14], forming stable Co compounds [2,15,16] and giving a suitable diffusion barrier layer on the substrates [17–22], etc., have been applied. Among them, selective etching of Co works fairly well for low cobalt content cemented carbides (e.g., WC–3 wt.% Co). However, when substrate contains higher concentration of Co, it requires strong etching by increasing the concentration of solution or the etching time in order to avoid the negative effect of Co. The

strong etching leads to a deep loose corrosion layer and deep pits of deficient Co on the substrate surface [23–25]. The removal of binder Co phase will also increase the roughness of surface, which directly leads to the reduction of the mechanical properties and applied range of the cutting tools. Moreover, a great concentration gradient of Co naturally occurs between corrosion layer and substrate interior. If the depth of corrosion layer is not enough, it will be difficult to avoid the cobalt diffusion from substrate interior to surface under diamond deposition condition [26].

In the present study, the WCGC has been reactively sputtered on WC–13 wt.% Co in various Ar–CH₄ gas mixtures prior the deposition of diamond films to act as a diffusion barrier against Co diffusion. The selection of WCGC as the interlayer started from the statement that: (a) W–C gradient layer should be homogeneous with respect to substrate, which not only can enhance the hardness, but also reduce the mismatch of interlayer and substrate; (b) the WC interlayer have a lower thermal expansion coefficient relative to other interlayer, which should be beneficial in reducing the mismatch arising from the thermal expansion coefficients difference between diamond and substrate; (c) tungsten can form a carbide bonding with carbon so that the formation of diamond crystal nucleus will be easier.

2. Experimental details

2.1. Deposition of W–C gradient interlayer

The substrate used in this work is the WC–13 wt.% Co with the size of 12 mm × 12 mm × 5 mm. The substrates were bombarded

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and cleaned with a Kauffman ion gun in order to eliminate the possible negative effects caused by the contaminants and adsorbed gas molecules. The discharging voltage was 70 V, with current of 1.25 A. The coil current was chosen as 6 A, whereas the acceleration voltage and current was set to 500 V and 40 mA, respectively. The gas atmosphere was Ar, with the pressure tuned to 0.5 Pa. The beam operation voltage was 1.5 kV, with a beam current of 78 mA. After the bombarding cleaning process, the WCGC layer was prepared by the DC magnetron reactive sputtering technique in a high vacuum chamber with an underground pressure less than 10^{-4} Pa. The purity of the tungsten target, argon gas and methane used was 99.99 wt.%, 99.99 vol.% and 99.999 vol.%, respectively. The substrate was grounded, no bias was applied. The pure tungsten layer was sputtered with the sputtering voltage and current of 400 V and 0.2 A, respectively. The sputtering pressure of the pure tungsten layer was 1.3 Pa. For the reactive sputtering of the WCGC, the sputtering voltage and current was 330 V and 0.4 A, respectively. The sputtering pressure was subsequently increased to 4.0 Pa for this process.

In our experiments, due to the fact that the coated samples must be returned to the ambient temperature amid the processes of PVD and CVD, and the sputtering devices can not perform at a temperature as high as that for the diamond deposition process, we determined that the sputtering process should take place at the half of the temperature range of the CVD diamond deposition (700–900 °C) to reduce residual compressive and tensile stresses. This temperature (400 °C) was chosen in a way that optimal adhesion and deposition rate can be achieved without having any crack or peeling.

The value of the methane partial pressure was optimized for the W–C gradient interlayer, where the optimized value was obtained by preparing and comparing samples with W–C interlayer deposited onto single crystal silicon (111) substrates under different CH_4 partial pressures. The partial pressures used for comparison were taken as 0%, 2.5%, 5%, 10%, 20% and 30%. It was found that for the samples obtained under the methane partial pressure higher than 10%, the composition of the deposited W–C layer did not change much, and further increasing in methane partial pressure can result in the formation of larger amount of amorphous tungsten carbide [27], thus we chose the optimized CH_4 partial pressure to be lower than 10%. The methane concentration was regularly changed as shown in Fig. 1 for the WCGC. The average thickness of deposited WCGC layer was around 10 μm for all samples.

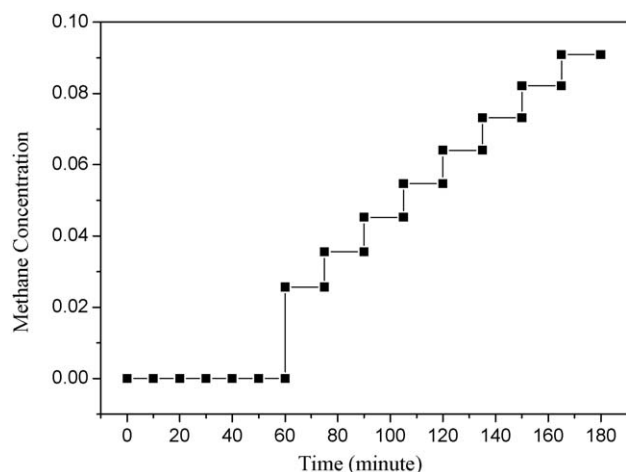


Fig. 1. The methane concentrations used during the PVD deposition of WCGC onto the WC–13 wt.% Co substrates.

2.2. Diamond deposition

Diamond film was deposited in a hot filament CVD reactor system consisting four parallel helix tungsten filaments mounted through molybdenum rod on a hydro-cooling copper frame. Prior to diamond film deposition, the tungsten carbide was etched for 60 s in mixed weakly acidic solution in an ultrasonic bath. Then the sample was abraded in an acetone-based ultrafine diamond suspension ultrasonically for 15 min. After an etching process in pure hydrogen was carried out for 10 min in CVD chamber, the methane was putted in. During the diamond growth the pressure was kept at 3.3 kPa, and the concentration of CH_4 was varied from 3% to 4%. The substrate temperature was set at 700, 800, and 900 °C, respectively.

The morphologies of the samples were inspected using a field emission SEM, Sirion200. The surface roughness and grain size distribution of the diamond films were determined by a commercial Solver P47 AFM. The XRD patterns were obtained from Dmax-2500VBX with Cu $\text{K}\alpha$ radiation, $\lambda = 0.154$ nm. The Dilor Super Labram with a typical resolution of $1\text{--}2\text{ cm}^{-1}$ in the back-scattering geometry was employed to investigate the bonding structures of the deposited films. The adhesion characterization of the diamond-coated WC–13 wt.% Co with WCGC was carried out by Rockwell hardness tester with diamond indenter (angle = 120°, radius = 0.2 mm) with 588 N load.

3. Results and discussion

Fig. 2 shows, respectively, XRD peaks of the sample of (a) as-received WC–13 wt.% Co substrate and (b) as-deposited WCGC. It is observed that after the deposition of WCGC the diffraction peaks match quite well with W_2C , but the diffraction peaks are significantly broadened. This may attribute to two aspects: (1) a layer of nanostructure WCGC was formed; (2) the WCGC maybe consist of multi-phases, since the position of the diffraction peaks of some phases are close to each other or even overlapped with each other, such as W, $\text{W}_2\text{C}_{0.85}$, $\text{W}_2\text{C}_{0.84}$, $\text{W}_6\text{C}_{2.54}$, $\text{W}_{12}\text{C}_{5.08}$, W_3C and WC_{1-x} . Because the CH_4 concentration was increased from 0% to 9% during the reactive sputtering deposition process, the prepared W–C coating will have a gradient structure [24,28].

The XRD patterns in Fig. 3 show the presence of W and W_2C phase after the deposition of WCGC, but no sharp WC diffraction peaks are clearly detected. Due to that fact that the WCGC are about 10 μm thick, it is very difficult for the X-ray to penetrate through the interlayer to detect the WC phase of WC–Co substrate. The XRD intensity of the WC phases (c.f., Fig. 3) is very strong, which indicates that the diffraction data for the peaks are mainly collected from the intermediate layer instead of the substrate. It is also demonstrated that, during HFCVD annealing for over 3 h at high substrate temperatures, the partial W_2C phase is transformed mainly into WC phases due to the diffusion of the active carbon atoms [24,29,30] (cf., Fig. 4). However, the diffraction peaks are narrower than that of PVD W–C gradient layer, which may be attributed to the formation of the very fine structure (nanos-structure) of the PVD WCGC.

The XRD patterns in Fig. 3(b and c) also indicate the crystal structure of diamond in the films, however in Fig. 3(a), the diamond peaks is not obviously resolved. For the two patterns in Fig. 3(b) and (c), an identical feature can be revealed with peaks at 2θ diffraction angle of 43.8°, which correspond to the (111) reflections of the cubic diamond. Other diffraction peaks of diamond, such as (220), (311), (400) and (331), can as well be observed correspondingly at 75.3°, 91.4°, 119.5° and 140.5°.

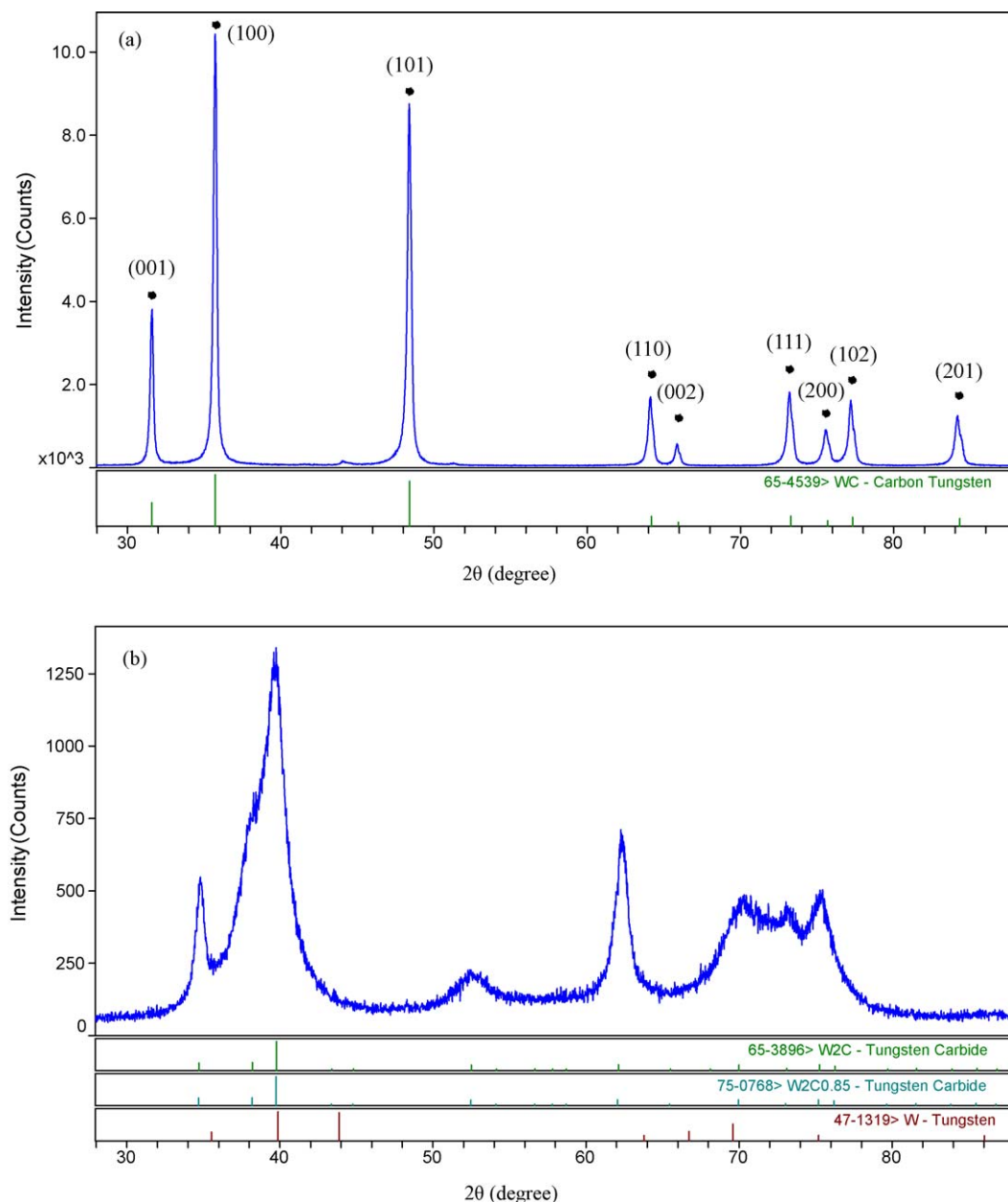


Fig. 2. The X-ray patterns of (a) the as-received WC–13 wt.% Co substrates and (b) as-deposited substrates with a WCGC.

However, it cannot be concluded that these diffraction peaks come from the diamond films, as the diffraction peaks of some phases are very close or even overlap with each other. In addition, the magnified X-diffraction patterns show that a small graphite peak is discernable at about 26.48° only when the substrate temperature was 700°C , revealing the presence of a possible small amount of crystalline graphite.

Because of the low electrical conductivity of the diamond films, it is difficult to observe clearly the morphologies of a diamond sample without a metal spraying using the conventional scanning electron microscope. In order to observe the original surface morphologies of nanocrystalline diamond films clearly and exactly, the field emission scanning electron microscope was employed. The FE-SEM surface micrographs of the diamond films deposited using different substrate temperature varied from 700 to 900°C are shown in Fig. 5(a–c). Specifically, the diamond film exhibits an ultra-fine structure when the substrate temperature

was 700°C . As the substrate temperature increases to 800°C , the size of the grains also increases and the morphology of grains are now spheriform. When the substrate temperature reaches 900°C , the morphologies of diamond grain are well-defined and the grain size becomes the largest among the three samples. The grains display as major planes of a pyramidal structure. The adjacent grains are close-packed and no gap is observed between the grains. The individual grains are very uniform and well-distributed on the surface of the film. Fig. 5(c) also shows a $\langle 1\ 0\ 0 \rangle \{1\ 1\ 1\}$ texture of the film and a typical “rough” morphology of the $\{1\ 1\ 1\}$ facets of the CVD diamond.

The corresponding surface 3D AFM images of the diamond films are shown in Fig. 5 (d–f). The grain size increases with the increasing substrate temperature, meanwhile the film surfaces become rougher. When the substrate temperature increases to 900°C , the surface of diamond film is the roughest and the grain size is also the largest, while the morphologies of diamond grain

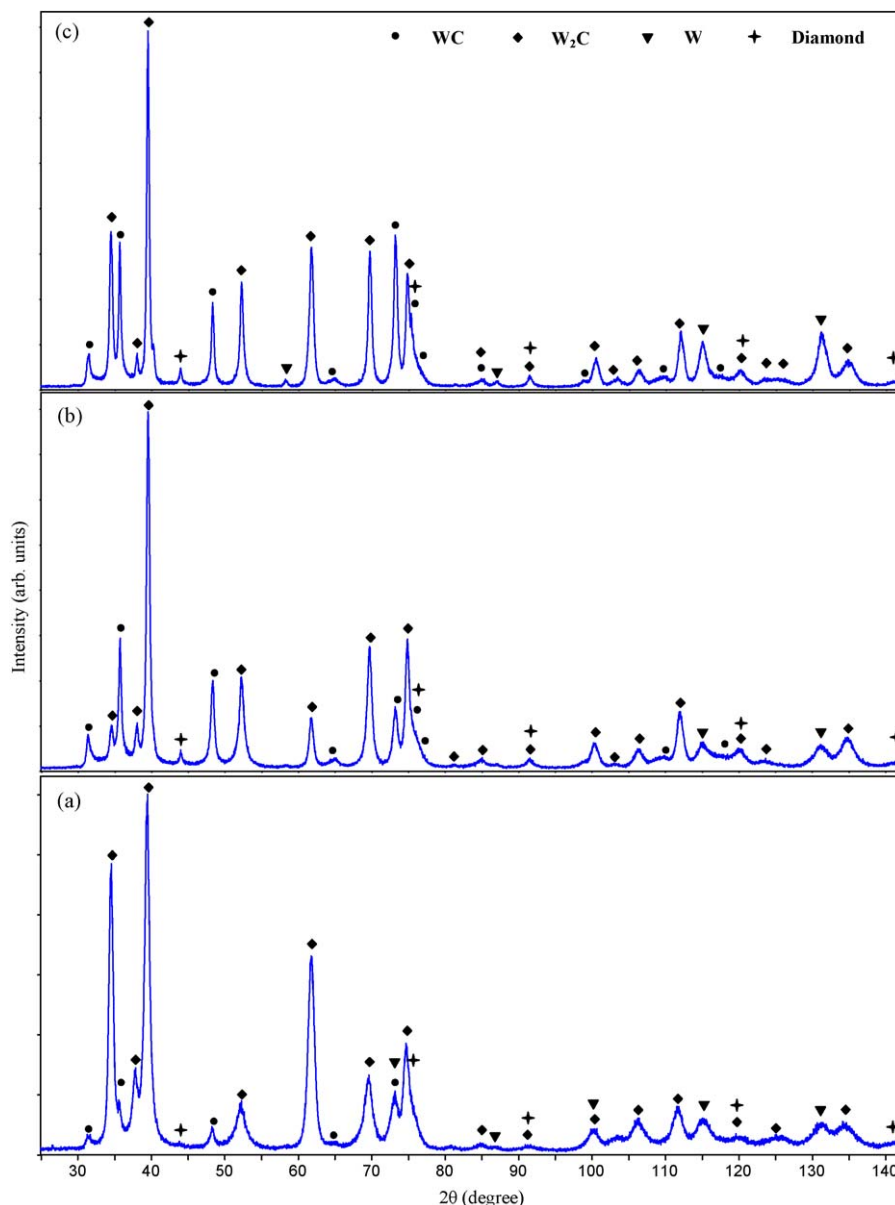


Fig. 3. The XRD patterns of the CVD diamond films deposited on WC–13 wt.% Co substrate with a WCGC at substrate temperature of (a) 700 °C, (b) 800 °C, (c) 900 °C.

are clearly resolved and the feature of most grains are homogeneous. The AFM topographic in a $3\ \mu\text{m} \times 3\ \mu\text{m}$ region displays a rough surface with the average surface roughness (R_a) of 22 nm, the root-mean-square roughness (RMS) of 27 nm, and the peak to peak distance (R_{max}) of 175 nm when the substrate temperature was 900 °C. When the substrate temperature was 700 and 800 °C, the R_a is 7 and 12 nm, the RMS is 10 nm and 15 nm; and the R_{max} is 67 nm and 107 nm, respectively.

The diamond grain size distribution can be coarsely approximated (c.f., Fig. 6) according to the AFM data. It is shown that nano-scaled particles are randomly distributed on the surface, and the grain size distribution obeys a Gaussian-like behavior, in the other word, the randomness of the size of the particles is identified. It can be observed that, the size of the diamond grains increases gradually with increasing substrate temperature. From the Gaussian fitting results, the Gaussian peak has a characteristic of peak position at 76 nm and its full-width-at-half-maximum (FWHM) is around 60 nm when the substrate temperature equals 900 °C. While for the

cases of the substrate temperature equals 700 and 800 °C, the respective peak position is at 31 and 49 nm, and FWHM is 19 and 34 nm, respectively. Of course, the grain size from the AFM images could be smaller than the real one because of the overlap of grains; however the qualitative description shown in Fig. 6 can readily reflect the law that govern the grain size distribution.

Raman spectroscopy is a convenient method for analyzing the carbon phase materials, as each phase yields specific peaks due to the characteristic vibration modes in that phase. In Fig. 7, the Raman spectra of the diamond films deposited at different substrate temperature (700, 800, and 900 °C) are displayed. The diamond films for these three samples exhibited a similar feature around $1335\text{--}1337\ \text{cm}^{-1}$ in the Raman spectra, corresponding to the characteristic peak of the diamond phase. However, all these peaks are slightly blue-shifted with respect to standard sp^3 peak ($1332\ \text{cm}^{-1}$). These shifts can be explained as the result of interface compressive stress due to the possible thermal stress and internal stress during the deposition processes. As substrate temperature

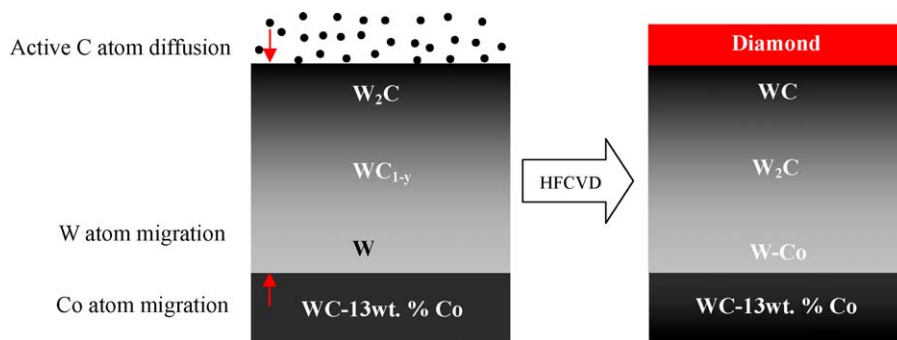


Fig. 4. Schematics of the phase transformation in the WCGC during the process of diamond deposition, WC_{1-y} , represents $W_2C_{0.85}$, $W_2C_{0.84}$, $W_6C_{2.54}$, $W_{12}C_{5.08}$, etc. ($0 < y < 1$).

increases, the peak intensity increases and the peaks become sharper, corresponding to higher concentration of diamond phase presenting in the substances. When the substrate temperature reaches 900 °C, the Raman spectra of the thin films has a sharp peak at 1336.8 cm^{-1} , which is close to the characteristic peak of

diamond at 1332 cm^{-1} , revealing high concentration and high quality of the deposited diamond film. Additionally, all samples are shown to have peaks in the range of 1400 cm^{-1} – 1600 cm^{-1} , which corresponds to the G-band of the non-diamond substances, the intensity of these peaks decrease with the increasing substrates

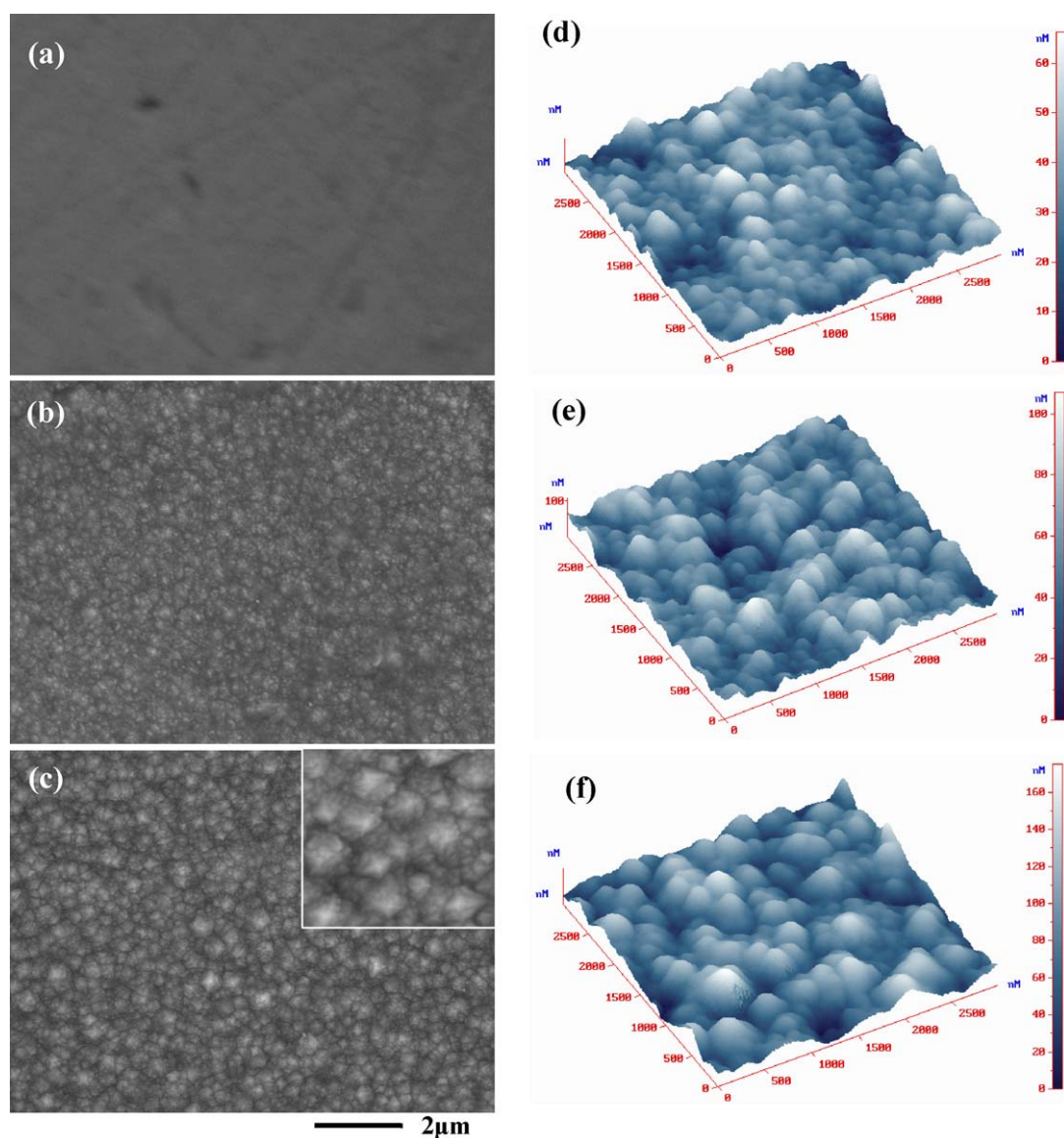


Fig. 5. The SEM morphologies and surface AFM images of the diamond films on the WC–13 wt.% Co substrates with the WCGC. The CVD deposition substrate temperatures are: (a and d) 700 °C, (b and e) 800 °C, (c and f) 900 °C.

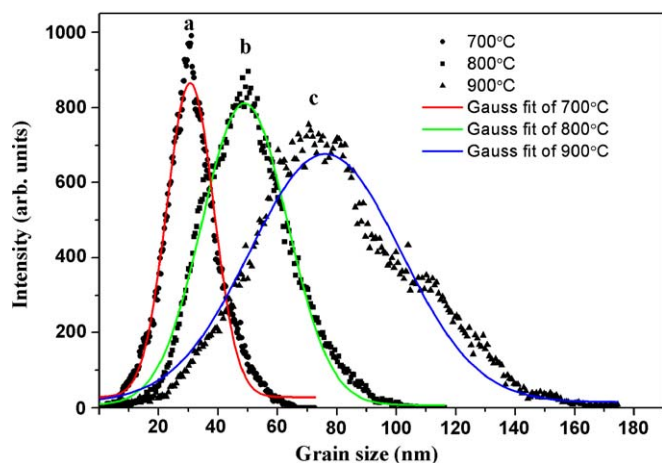


Fig. 6. The size distribution of the diamond grains in the films grown on the WC–13 wt.% Co substrates with the WCGC at different CVD deposition substrate temperature: (a) 700 °C, (b) 800 °C, (c) 900 °C.

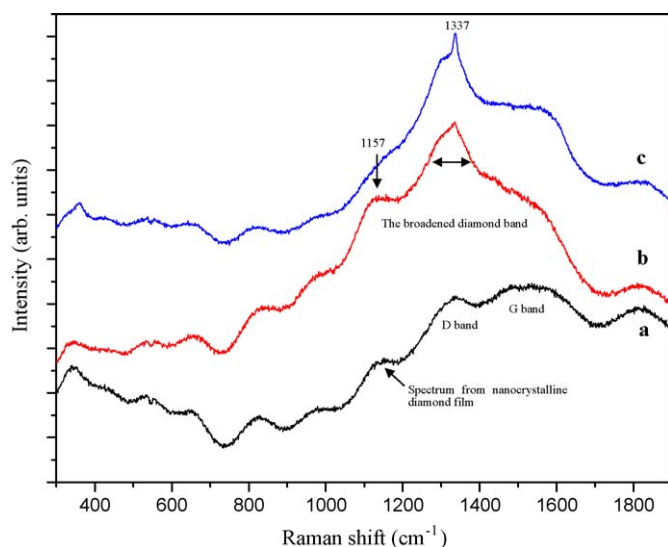


Fig. 7. The Raman spectra of the diamond films deposited on the WC–13 wt.% Co substrates with the WCGC using for different CVD deposition substrate temperature: (a) 700 °C, (b) 800 °C, (c) 900 °C.

temperature, which suggests the reduction of sp^2 hybridization of carbon in the diamond films and the improvement of the quality of the diamond films with increasing substrate temperature. This hypothesis is also supported by the fact that the higher substrate temperature favors the hydrogen etching process of graphite and improved generation of activated hydrocarbon radicals can promote the diamond nucleation and deposition as well. Special attention should be paid to the additional peak ranging from 1100 cm^{-1} to 1200 cm^{-1} . The additional peak becomes less observable with the increasing substrate temperature. Combining the XRD, SEM and AFM results, it can be concluded that this peak is mainly contributed from the size effect of nanoscale diamond grains, which is also confirmed by other researches [31,32].

A Rockwell indentation test with a load of 588 N was conducted to evaluate the adhesion of the films, where three diamond films grown at different substrate temperatures: 700, 800 and 900 °C were investigated; the SEM images of the tested samples are shown in Fig. 8. From the SEM results, serious peeling and long length cracks can be observed for the indented film grown at a lower substrate temperature of 700 °C. With increasing substrate temperature, the amount of peeling and crack decreases obviously.

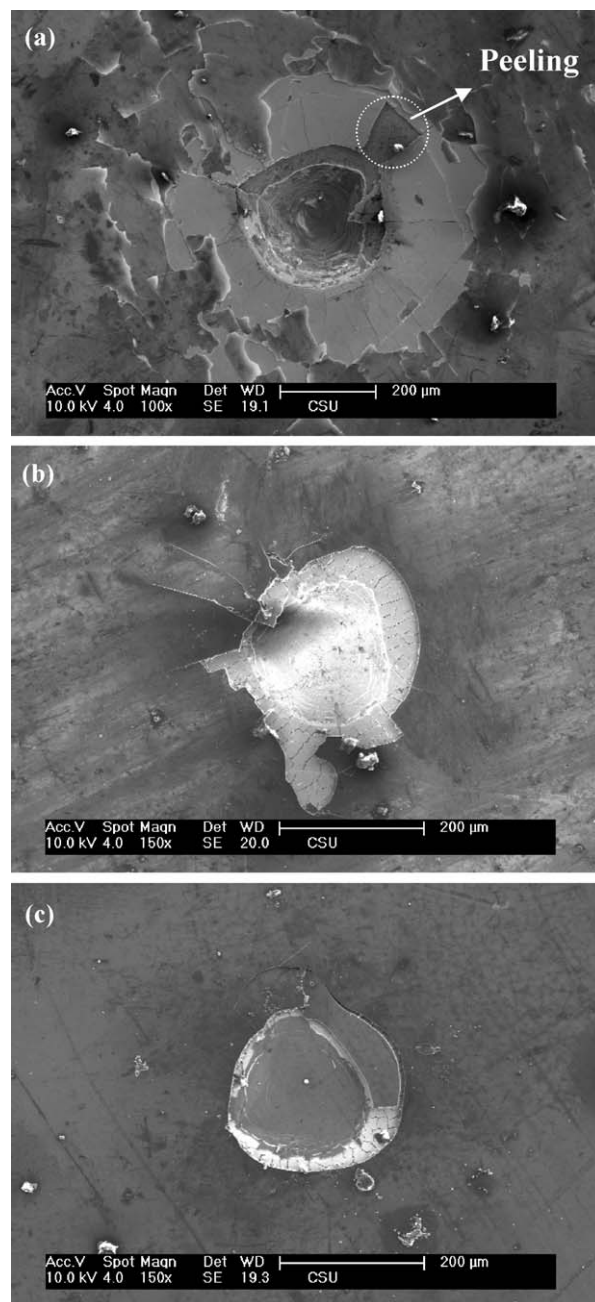


Fig. 8. The morphologies of the Rockwell indentations on the diamond films under a load of 588 N. The CVD diamond films were deposited at (a) 700 °C, (b) 800 °C, (c) 900 °C, respectively.

Especially when the substrate temperature reaches 900 °C, the diamond-coated WC–13 wt.% Co with the WCGC shows the shortest crack length, smallest impress diameter and least amount of peeling compared to that of 700 and 800 °C.

Usually during the conventional diamond CVD processes, the higher the substrate temperature, the larger the thermal stress, thus the poorer the adhesion. However, for the diamond films deposited at high temperature in our experiments, they have better adhesion properties compared to that of low temperature case, this can be ascribed to the fact that the migration of Co from the interior of the substrate to the interface of the WCGC is faster at higher temperature, which extremely increases the adhesion between interlayer and substrate due to the formation of stronger bonding, which is also supported by comparing the samples

prepared at different substrate temperature. An obvious peeling of WCGC can be observed in Fig. 8(a), but Fig. 8(b and c) tells quite different stories. Moreover, the diffusion of the active carbon atoms becomes faster at higher substrate temperature, which favors the phase transformation from W_2C to WC (cf., Fig. 3); finally the enhancement of the nucleation of the diamond films can be achieved. The quality and adhesion of diamond films would be further improved by providing an adjustment of the WCGC stoichiometry and the microstructure therein such as the phase composition and the thickness of each layer.

4. Conclusions

In this work, the substrate temperature on the nucleation, smoothness, quality and adhesion of polycrystalline diamond films grown by hot-filament CVD on WC–13 wt.% Co substrates with the WCGC is investigated. (a) During HFCVD annealing, the superficial W_2C phase of the WCGC is transformed mainly into WC phases due to the diffusion of the active carbon atoms, which are favorable for enhancing the nucleation of diamond film; (b) well-crystallized diamond films with large grain size have good adhesion with the substrates, though they are usually rougher than those poor crystallized with small grain size, which exhibit a smooth surface, yet, with poor adhesion and chemical property; (c) the WCGC can play a role of effective barrier that can prevent Co diffusion from substrate interior to the surface, resulting in good adhesion of diamond film to the substrate.

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