Physical Properties of Diamond Coatings on a WC-6%Co Substrate *

LIU Sha(刘沙), YI Dan-Qing(易丹青), YU Zhi-Ming(余志明)
Department of Materials Science & Engineering, Central South University, Changsha 410083

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We have investigated the physical properties, including the morphology, texture, adhesion and chemical quality, of high-frequency chemical vapour deposited diamond coatings on WC-6%Co substrates, which were pre-treated by a two-step etching method. The results indicate that the increasing Co content from 0.12 to 3.05% within the etching depth of 5 μm caused a morphology transformation from prism diamond to spherulitic diamond, and a texture transformation from a {111} orientation to a {110} orientation. The Raman spectrum shows that the spherulitic diamond film contains more non-diamond phases (graphite, amorphous carbon and diamond-like carbon, etc) and has lower chemical quality than diamond films on a WC-6%Co substrate. The diamond coating grain sizes became about four times smaller when the deposition temperatures on the substrate surface were reduced from 1000 to 900°C. Compared with spherulitic diamond films, the prism diamond films exhibit better adhesion on the WC-6%Co substrate.

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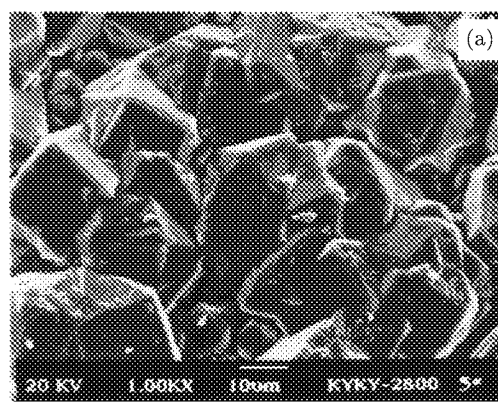
Diamond by chemical vapor deposition (CVD) has shown its potential applications as a cutting coating and has begun to play an important role in industrial material machining. Compared to uncoated cemented carbides, diamond-coated carbides can prolong the lifetime of tools by three to ten times and greatly raises the value of the product. Since there is a large difference in physical and chemical properties between cemented carbides and diamond, a breakthrough of diamond-coated cutting tools has not taken place so far, although deposition processes for diamond have been well known for more than a decade. There are two key problems that hamper the development of the high-quality products. One is low adhesion between substrates and the diamond film. The other is the fact that it is difficult to control the microcrystalline nature of diamond films. It is well known that the cutting performance of diamond-coated tools is influenced by the microcrystalline natures of diamond films which are sensitive to the surface pre-treatment and deposition procedures.[1−10] Therefore it is significant to study the physical properties of diamond coatings on WC-6%Co for controlling the microcrystalline nature of diamond films.

In this Letter, we try to determine the correlation between the Co content in the substrate surface and CVD deposition temperature by investigating the physical properties of diamond coatings, so as to deposit the high-quality diamond films by controlling the pre-treatment and deposition conditions.

The substrate samples of WC-6% Co with dimensions of $9.0 \times 5.5 \times 3.0\,\mathrm{mm}^3$ were pre-treated with two-step etching methods. A hot-filament reactor, as described elsewhere,[11] was used for the deposition of diamond film. The temperatures at the substrate surface were at 900−1000°C during the deposition process. The morphologies of the diamond film were observed by a scanning electron microscope KYKY-2800. An x-ray diffractometer (Siemens D-5000) was applied to examine the crystal structure. A Spex 1403 macro-Raman spectrometer was used for chemical quality evaluation by Raman characterization. A Rockwell indenter was used to determine the adhesion between the substrate and diamond films.



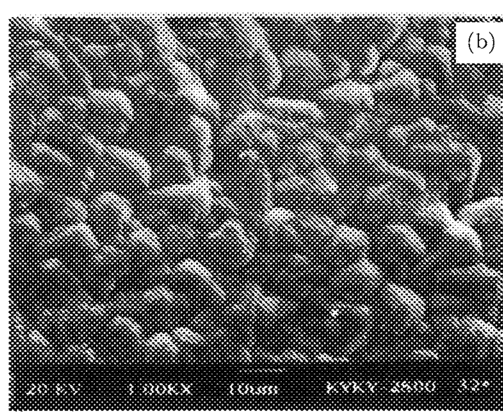


Fig. 1. SEM images of prism (a) and spherulitic (b) diamond films on WC-6%Co samples.

Two samples, which have Co contents of 0.12% and 3.05%, with an etching depth of 5 μm on the substrate surface, were obtained by the two-step etching method, using different etching times of second step followed by high-frequency (HF) CVD.[12] The sample morphology with a Co content of 0.12% looks like the prism diamond shown in Fig. 1(a), while the sample

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with Co content of 3.05% shows a spherulitic morphology, as illustrated in Fig. 1(b). According to the Co–C phase diagram, C can be dissolved in the Co phase. The more the Co content on the substrate surface, the more the C content in the surface. Under the same deposition conditions, the different morphologies of diamond films emerged because of the different Co contents on the substrate surface.

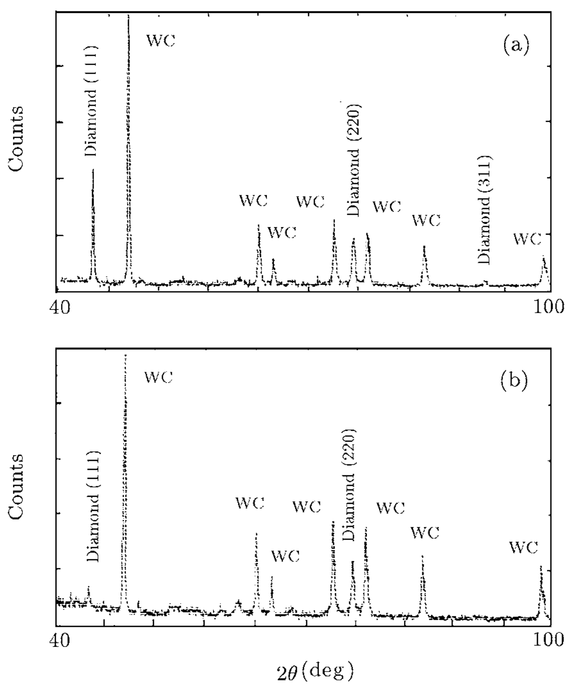

Fig. 2. XRD patterns of prism (a) and spherulitic (b) diamond film on WC-6%Co samples.

Figure 2 shows the XRD patterns of the above diamond films on the WC-6%Co samples. A slight preference towards {111} orientation can be observed in Fig. 2(a), since the peak of {111} orientation is higher than others, while the other sample shows a preference towards {110} orientation, as shown in Fig. 2(b), because the peaks of {110} orientation are higher than those of {111} orientation. The preference towards a certain orientation of diamond films is closely related to the values of surface free energy, which are affected by many factors in which the composition of the substrate surface plays an important role. This is the same reason as mentioned above for the different forms of diamond film morphology, which leads to the different preferences towards certain orientations.

The purity of the diamond phase is detected by Raman spectrum analysis. The standard Raman spectrum peak of the diamond phase is at about $1332\pm4\,\mathrm{cm}^{-1}$, while the Raman spectrum peaks of non-diamond phases (graphite, amorphous carbon, diamond-like carbon, etc) are at about $1500-1700\,\mathrm{cm}^{-1}$. The higher the peak of the diamond phase, the purer the chemical quality of the diamond phase.

Figure 3 shows the Raman spectra of the prism (a) and spherulitic (b) diamond films on WC-6%Co samples. It is shown that the chemical quality of the prism diamond film with the peak at $1332\,\mathrm{cm}^{-1}$ is purer than that of the spherulitic diamond film. It also shows that the spherulitic diamond films contain more non-diamond phases and have higher intrinsic stress.

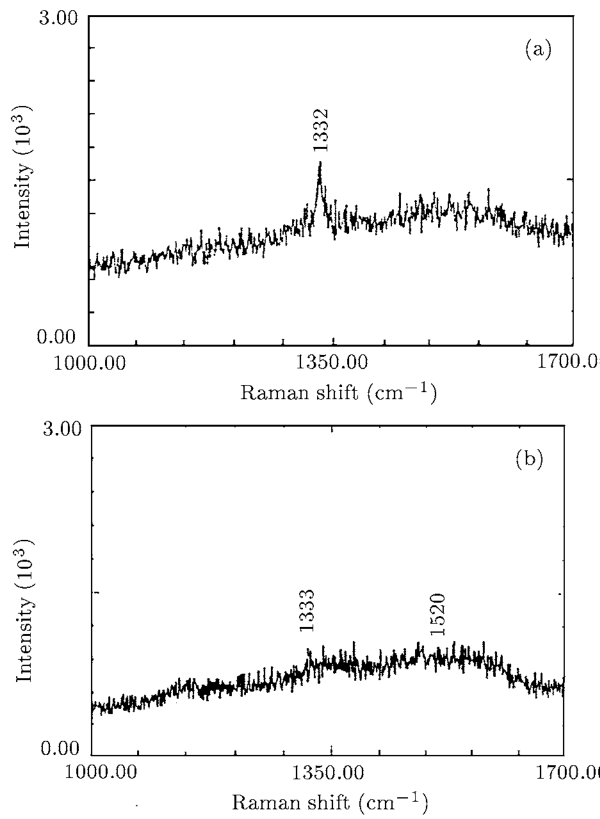

Fig. 3. Raman spectrum of the prism (a) and spherulitic (b) diamond films on WC-6%Co samples.

The indentation tests allow the evaluation of film adhesion in terms of the coating-substrate interface toughness, according to the following mathematical description[13]

$$R(P) = \alpha[1 - P_c/P]^{1/2}P^{1/4},$$

where

$$\alpha = \alpha_1 t^{3/2} H^{1/2}(2\pi K)^{-1},$$

α_1 is a numerical constant, t is the coating thickness, H is a mean hardness, P_c is the critical stress for the crack propagation, K is the indentation fracture toughness parameter, P is the applied load, and R is the measured crack radius.

Indentation test results were interpreted by analysing the SEM images of the damage produced in the diamond films. The smallest load is necessary to produce the first cracks for measurement of the film adhesion.[14]

The SEM images of the imprint obtained by Rockwell (60 kg) indentations of the prism and spherulitic diamond films grown on the WC-6% Co substrates are shown in Figs. 4 (a) and 4(b), respectively. It is clear from Fig. 4 that, in comparison with the spherulitic diamond films, the prism coatings did not result in any cracking expansion and had a smaller crack radius at the same Rockwell load. This means that the prism diamond films exhibit better adhesion on the substrates because the spherulitic diamond films have higher intrinsic stress, as in the above-mentioned Raman spectrum results.

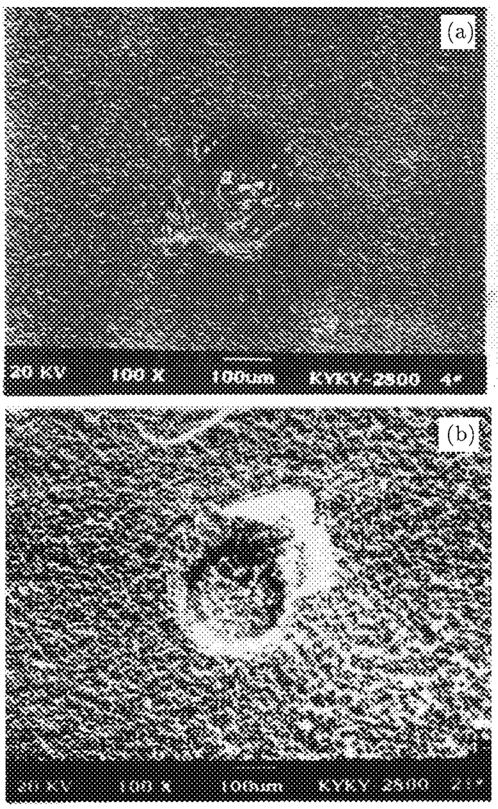

Fig. 4. SEM images of the imprint obtained by Rockwell (60 kg) indentations of the prism (a) and spherulitic (b) diamond films grown on the WC-6%Co substrates.

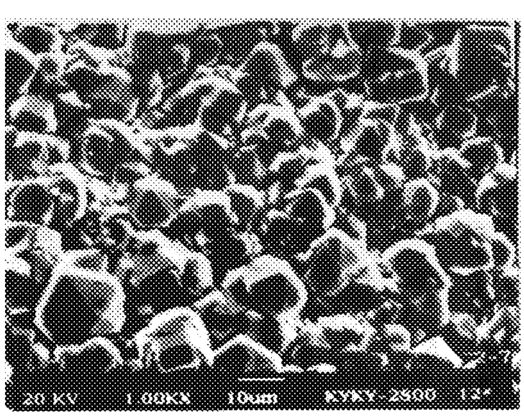

Fig. 5. SEM image of diamond films with the deposition temperature of 900°C on WC-6%Co samples.

The grain sizes of diamond coatings are important to the cutting performance of diamond-coated tools. In order to perform fine machining and finishing, the fine grain sizes of diamond coatings should be gained by controlling the deposition conditions. According to thermodynamics conditions,[15] the lower the deposition temperature, the smaller the grain sizes. However, the diamond grains gradually lose their crystalline form and switch to an amorphous-like morphology when the deposition temperature is lower than a critical value. The diamond coatings grains of 5-10 μm were obtained at the deposition temperature of 900°C, as shown in Fig. 5. Under the same deposition conditions, compared with the grain sizes at the deposition temperature of 1000°C, as shown in Fig. 1(a), it is observed that the grain sizes become about four times smaller. The growth regulation of diamond grains is very similar to that of ordinary crystal and sensitive to the deposition temperature. Therefore, further experiments at the lower deposition temperatures should be done in order to reduce the grain sizes of diamond films on WC substrates.

In summary, we have investigated the physical properties, including morphology, texture, adhesion and chemical quality, of HF CVD diamond coatings on a WC-6%Co substrate which were pre-treated by a two-step etching method. Based on the experimental results, the following conclusions can be drawn. Increasing the Co content from 0.12 to 3.05% within the etching depth of 5 μm can cause a morphology transformation from prism diamond to spherulitic diamond, and a texture transformation from a {111} orientation to a {110} orientation. The Raman spectrum shows that the spherulitic diamond film contains more non-diamond phases and has lower chemical quality of diamond films on a WC-6%Co substrate. The diamond coating grain sizes become about four times smaller when the deposition temperatures on the substrate surface are reduced from 1000 to 900°C. Compared with spherulitic diamond films, the prism diamond films exhibit better adhesion on the WC-6%Co substrate.

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