Diamond formation on carbon/carbon composite

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A carbon/carbon composite was used as substrate for low-pressure diamond deposition. To enhanced diamond nucleation on carbon/carbon composites, a total of ten surface preparation methods have been investigated. These methods involved the use of atomic hydrogen etching, mechanical polishing, sonication, or coating. Diamond nucleation was found to occur on either the defects of the carbon/carbon composite substrates or diamond particulate left on the substrates. The defects were created primarily by atomic hydrogen etching during the coating process. Seeding with diamond powders was performed by dip coating, sonication, or spray-coating processes. It was found that these seeding processes resulted in excellent nucleation of diamond.

1. Introduction

It is known that diamond formation on various substrate materials can be enhanced by scratching, sonicating, or seeding the surfaces with abrasive powders. Among these abrasive powders, diamond dust has been found to be the most effective one [1]. Other surface preparation methods such as bias-enhanced nucleation [2], seeding with carbon clusters [3], the use of various intermediate layers [4], and coating with hydrocarbon oil [5], have also been used to enhance diamond nucleation on the substrate surface. These methods, especially the use of diamond dust for scratching and/or seeding, are commonly used on substrate materials such as silicon, molybdenum, nickel, copper, SiC, c-BN, WC, and AlN. The use of carbon materials as substrates has received less attention.

The mechanism of enhancing diamond nucleation on silicon by using diamond dust has been proposed to be the introduction of diamond fragments and micro-scratches [1]. These diamond fragments, as well as the micro-scratches, served as the nucleation sites for diamond formation. Compared to the surface of the silicon substrate generally used for diamond deposition, the surface of a carbon/carbon composite is less dense and contains small pores which could make pin-hole-free diamond film difficult to obtain. In addition, depending on the architecture of the reinforcing fibres, different surface topologies exist. The nucleation of diamond has been found to be influenced by substrate topology, such that prominent features are favoured for the nucleation [6]. In this study, we have used a carbon/carbon (CC) composite as substrate for diamond formation. Diamond formation on carbon/carbon composite can electrically passify the composite. Various routes of surface preparation were examined.

2. Experimental procedure

The carbon/carbon composite used in this study was acquired from BFGoodrich Aerospace (Santa Fe Spring, CA, USA). This type of composite has three-dimensional fibrous reinforcement with highly graphitic matrix carbon. The reinforcing fibres were PAN (polyacrilonitrile) fibres. It is noted that the matrix carbon exhibits microstructure in which the prism plans were arranged to be parallel to the fibres. A number of surface treatment methods was employed to prepare the as-received CC composite for diamond deposition. These methods are summarized in Table I. Abrasive diamond dusts obtained from different sources were used. The average sizes of these diamond dusts vary. All the specimens were cut from the same piece of as-received CC composite. All the surface treatments were then performed on as-cut CC composite specimens. For comparison, as-cut specimen without any pre-treatment was also used. In addition, it was anticipated that by using etching for surface treatment, more nucleation sites could be obtained as a result of more defects being exposed.

For diamond deposition, a microwave plasma-enhanced chemical vapour deposition (MPECVD) technique was used. The microwave system utilizes an ASTEX HS-1000 magnetron with an S-1000 Control Unit/Power supply to produce up to 1 kW 2.45 GHz microwave power. Microwave power is tunable via an ASTEX TS three stub tuner. An ASTEX CS circulator and a water-cooled ASTEX LS dummy load are used to isolate the magnetron head from any reflected power. An ASTEX directional coupler is used to monitor reflected power. A custom-built water-cooled applicator (ASTEX PA25A) permits insertion of a 3.81 cm (1.5 in) o.d. quartz reaction tube to pass through the waveguide. Gas is introduced at the top of the reactor tube, and is evacuated at the bottom. Gas flows are controlled with a four-channel MKS Multi-Gas Controller. The deposition conditions used for all the specimens were the same: $H_2/CH_4 = 0.1$ standard cm^3 $min^{-1}/99$ standard cm^3 min^{-1}, pressure 30 torr, temperature 1050–1075 °C, and deposition time 20 h. After the deposition, specimens were characterized

TABLE I Methods used for surface preparation prior to diamond deposition

Method	ID	Description
None	1	As-cut specimen.
Etching	2	Etched in the microwave reactor under the conditions of 100 standard $cm^3 min^{-1}$ H_2, 30 torr, and 1050 °C.
Polishing A	3	Polished by 600-grid SiC paper.
Polishing B	4	Polished by Metadi II[a] 1 μm diamond paste.
Dip coating A	5	Dipped in furfuryl alcohol then dried in air.
Dip coating B	6	Dipped in (diamond compound A[b] + furfuryl alcohol) then dried in air.
Dip coating C	7	Dipped in (diamond compound B[c] + furfuryl alcohol) then dried in air.
Dip coating D	8	Dipped in (diamond compound B[c] + water) then dried in air.
Sonication A	9	Sonicated in (diamond compound A[b] + water) then rinsed with water and dried in air.
Sonication B	10	Sonicated in (diamond compound B[c] + water) then rinsed with water and dried in air.
Spray coating	11	Sprayed with Dia-Silk[d] (Grade 1/4) then dried in air.

[a] Buehler, Lake Bluff, IL.
[b] Diamond compound made with GE 300S synthetic diamond powder. Size 0–0.5 μm. Warren Diamond Powder Co., Inc. Olyphant, PA.
[c] Diamond compound made with GE 300S synthetic diamond powder. Size 0–2 μm. Warren Diamond Powder Co., Inc. Olyphant, PA.
[d] Diamond suspension. Warren Diamond Powder Co., Inc. Olyphant, PA.
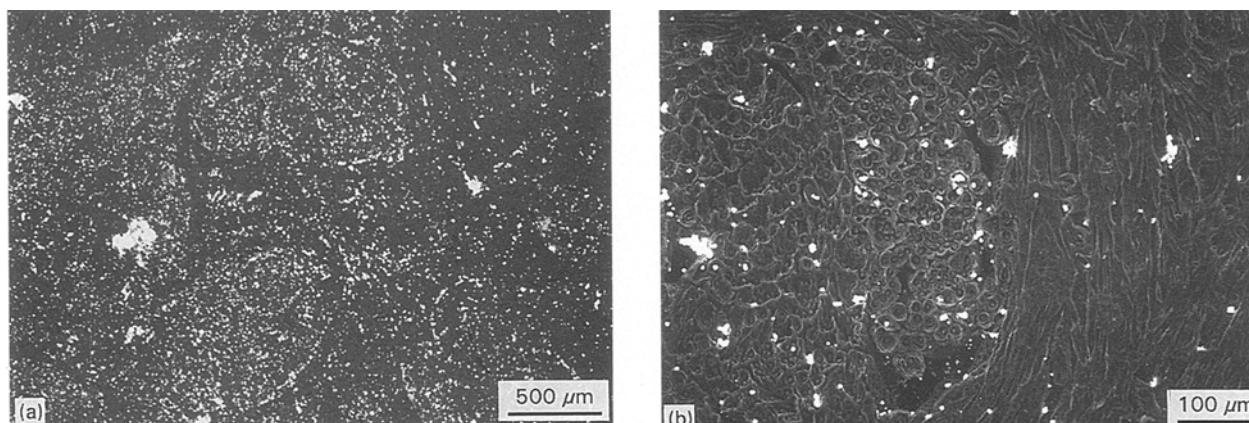

Figure 1 Diamond deposit on as-cut composite specimen showing (a) low nucleation density, and (b) severe etching of the specimen.

using scanning electron microscopy (SEM) and micro-Raman spectroscopy.

3. Results

Fig. 1 shows diamond coatings on a specimen prepared using Method 1. Spotty diamond nucleation on the specimen is seen in Fig. 1a. As indicated by the surface morphology shown in Fig. 1b, the composite specimen has been severely etched. No preferred crystal orientation was found for the coatings. For specimen prepared using Method 2, the nucleation density appears to be higher than that of the above specimen. It appears that nucleation occurred homogeneously on the specimen surface as shown in Fig. 2. For specimens prepared using Methods 3, 4 and 5, nucleation densities similar to that of specimen prepared using Method 2 are obtained. An example is given in Fig. 3 which shows scanning electron micrographs of a specimen prepared using Method 4. Also shown in Fig. 3 is the preferential nucleation of diamond. The preferred diamond nucleation sites were found to be the severely etched matrix carbon. This is shown at higher magnifications in Fig. 4.

For specimens prepared using Methods 6–11, it appears that the nucleation sites are no longer "intrinsic"
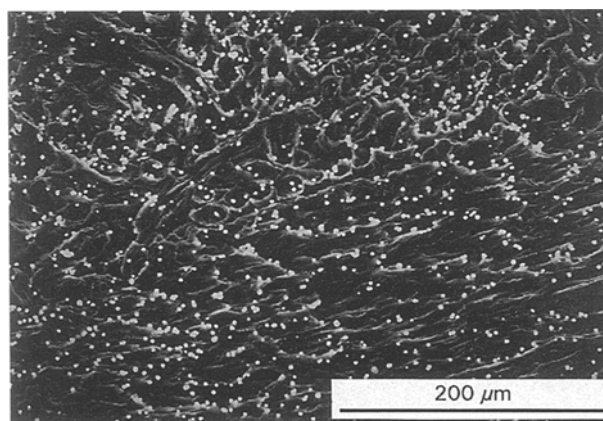

Figure 2 Diamond deposit on a specimen prepared using Method 2. It appears that nucleation occurred homogeneously on the specimen surface.

but "foreign species". The general morphologies of diamond coatings on these specimens are shown in Fig. 5. The nucleation densities are much higher than all those of the aforementioned specimens. Diamond nuclei grew and collided by the end of deposition so that localized continuous coatings were obtained on the majority of specimen surfaces, except for the specimen prepared using the spray-coating process
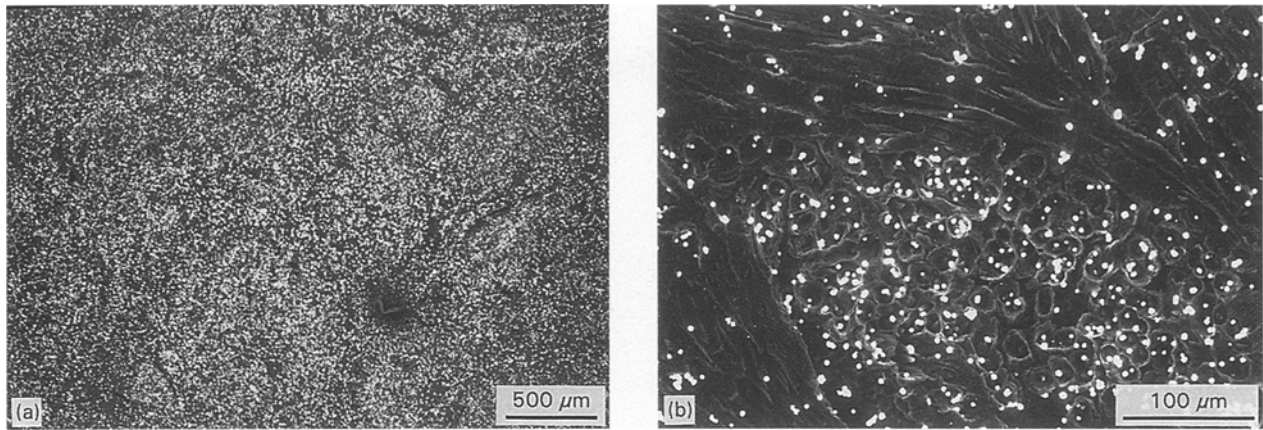
Figure 3 Diamond deposit on a specimen prepared by Method 4 showing (a) a higher nucleation density, compared to Fig. 1a, and (b) preferred nucleation sites.
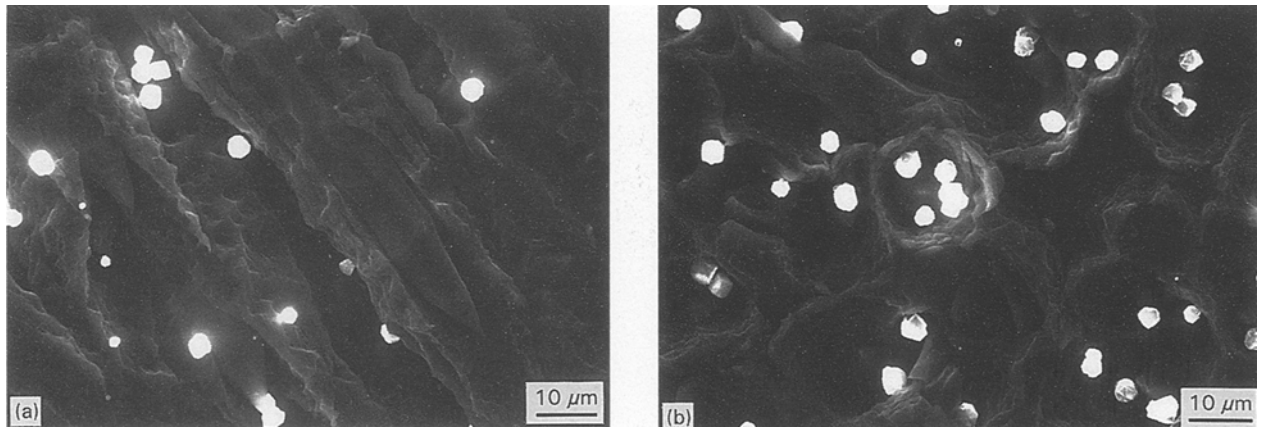

Figure 4 The preferred nucleation sites shown in Fig. 3b are the severely etched matrix carbon. (a) Matrix carbon surrounding fibres parallel to the paper. (b) Matrix carbon surround fibres perpendicular to the paper.

(Method 11). The discontinuity or pores on the specimen surfaces were found to be a result of the porous nature of the composite used. However, diamond formation occurred inside the pores as shown in Fig. 4e and 4f, indicating continuous coatings on the entire surface can be obtained on a dense surface. Islands of diamond coatings were found on a specimen prepared using Method 8 due to the poor dispersion of diamond powder in water (Fig. 5c). Fig. 6 shows microstructure of the coatings on specimens prepared using Methods 6–11. Diamond crystals with preferred orientation of (100) seem to dominate in most of the cases. Micro-Raman analysis was performed for the coatings shown in Fig. 6. All the spectra exhibit the characteristic peak of diamond near 1332 cm^{-1}. Typical spectra are given in Fig. 7, which were taken on the specimen shown in Fig. 6a.

4. Discussion

Using carbon materials (excluding diamond) as substrates for low-pressure diamond deposition, may be undesirable following the Russian school of thought that carbon materials will be severely etched by atomic hydrogen [7, 8]. Recent reports have indicated that the formation of diamond on graphite is possible, but not favourable, excepting on edge planes [9–11].

In the current study, diamond nucleation or formation was observed on carbon/carbon composite specimens with or without surface pre-treatment. Depending on the surface preparation, various degrees of diamond deposition were obtained. In general, the coating mophologies can be categorized into two groups as shown in Figs 1–4 for one group, designated Group A, and Figs 5 and 6 for the other group, designated Group B. The major differences between these two groups are the nucleation sites and nucleation densities of diamond.

It appears that different specimen preparation methods used for Group A specimens did not result in different deposition. These methods lead to higher nucleation densities as compared to that of the as-cut specimen. However, the previous argument [1], suggesting diamond nucleation was enhanced due to the presence of scratches or abrasive fragments, does not apply. It was found that Group A specimens were severely etched and the atomic hydrogen attacked the PAN fibres greater than the matrix carbon. As a result, the diamond nucleation occurred mostly on the etched matrix carbon, as shown in Fig. 4. On the other hand, the aforementioned argument seems to apply for diamond deposition on Group B specimens. The nucleation density was apparently enhanced due to the introduction of various diamond powders. For
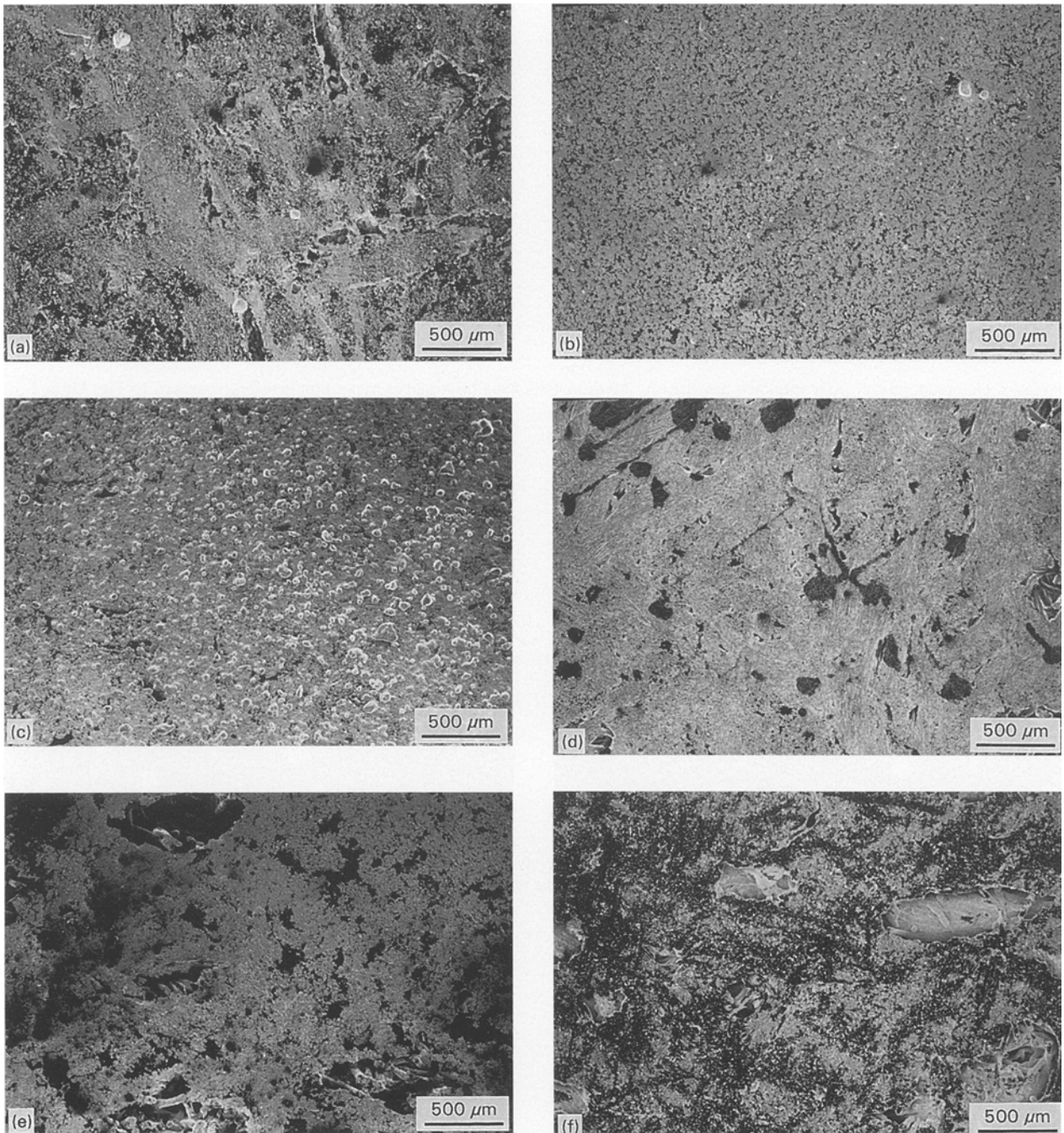
Figure 5 Surface morphologies of specimens prepared using (a) Method 6, (b) Method 7, (c) Method 8, (d) Method 9, (e) Method 10, and (f) Method 11.
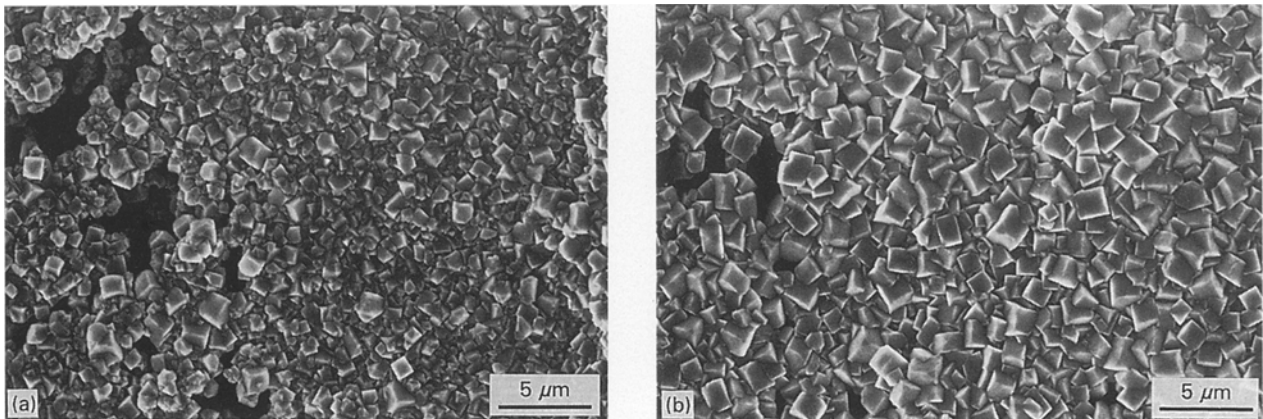

Figure 6 Microstructure of the coatings on specimens prepared using (a) Method 6, (b) Method 7, (c) Method 8, (d) Method 9, (e) Method 10, and (f) Method 11.
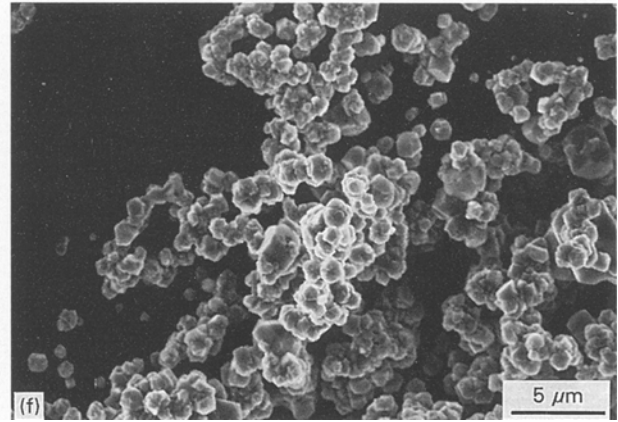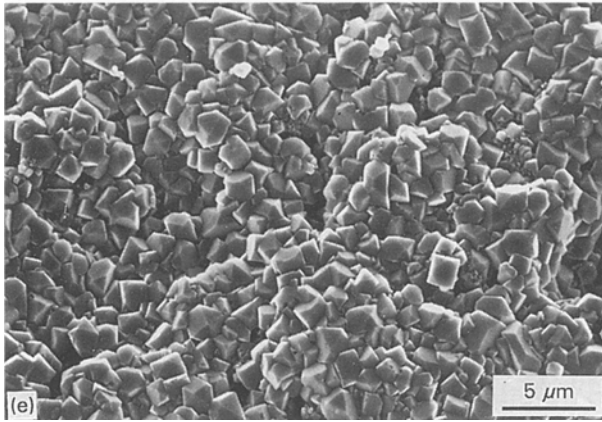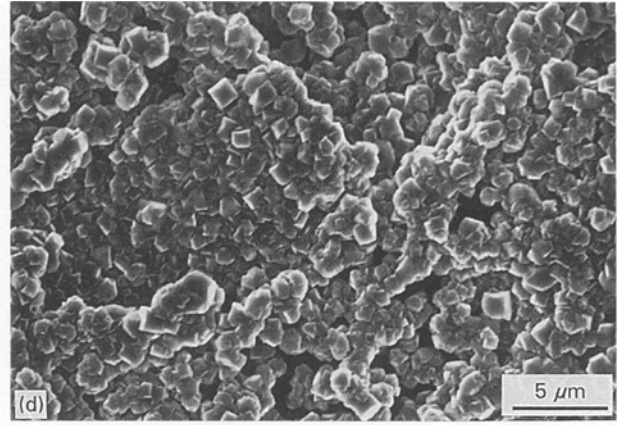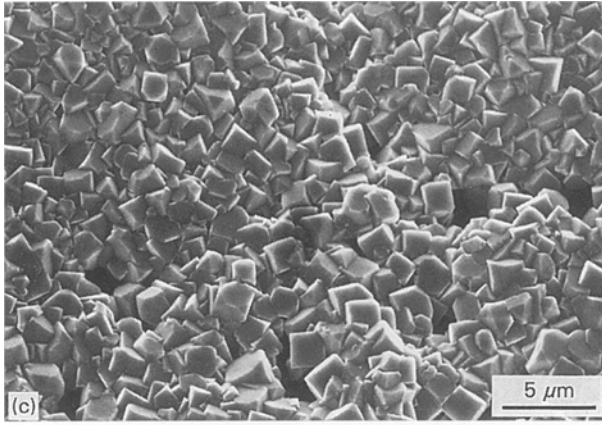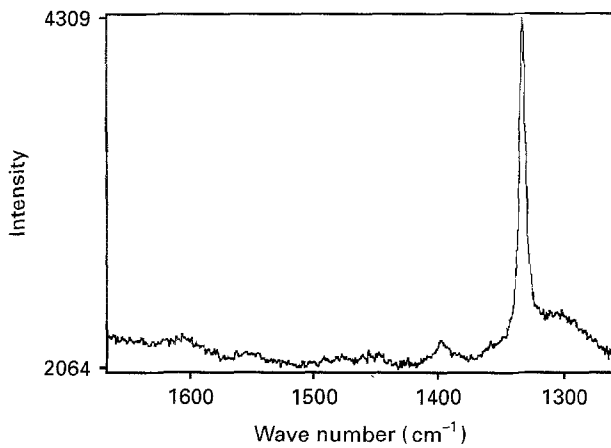
Figure 6. Continued

Figure 7 Raman spectra obtained from the coatings shown in Fig. 5 exhibit the characteristic peak of diamond near 1332 cm^{-2}. The spectrum given was taken on the specimen shown in Fig. 5a.

these specimens, the diamond crystal sizes are affected by the sizes of diamond powders. This further supports the formation of diamond on the powders used. The average crystal sizes shown in Fig. 6a–e are 1.0, 1.5, 1.6, 0.9 and 1.4 µm, respectively. The fact that the (1 0 0) surface dominates is beneficial as the probability of defect incorporation and twin formation is much lower than when the (1 1 1) surface dominates [12], and (1 0 0) surfaces have a higher resistance to etching [13].

Previous studies using carbon fibre as the substrate have demonstrated that diamond formation competed with etching of substrate fibres such that diamond

nucleation on more graphitic fibres was favoured [14, 15]. A similar kinetic competition also occurs when CC composite is used as substrate. It is proposed that an incubation period at the beginning of the deposition process may exist. During the incubation time, carbon from the CC composite surface is etched by atomic hydrogen while carbon from the gas phase selectively arrives on favourable nucleation sites. If the surface cannot provide enough favoured and stable nucleation sites, poor or no nucleation is found. It is noted that while atomic hydrogen etches the specimen surface, it also generates favoured nucleation sites and therefore leads to the exposure of the edges of prism planes. This accounts for the diamond nucleation on the as-cut specimen (Fig. 1). Further evidence supporting the generation of nucleation sites by atomic hydrogen etching can be realized by comparing Figs 1 and 2. The specimen shown in Fig. 2 was etched by atomic hydrogen prior to the deposition. This resulted in a higher nucleation density (Fig. 2) than that of the as-cut specimen (Fig. 1). For specimens prepared by polishing (Methods 3 and 4), due to the unstable condition of the substrate surface (resulting from atomic hydrogen etching), the scratches and/or possibly fragments left fail to serve as nucleation sites. Instead, the specimens again relied on atomic hydrogen etching to create favourable nucleation sites. For the Group A specimen, it is believed that the number of nucleation sites was insufficient and diamond nucleation and growth time was limited due to the incubation. These have contributed to the

fact that diamond crystals did not grow sufficiently to collide and also failed to develop any preferred orientation by the end of deposition.

The nucleation sites can also be generated by introducing a sufficient amount of high-purity diamond powder which has a higher resistance to etching than carbon [16]. For specimens in Group B, owing to the presence of high-purity diamond powders, the kinetics of diamond nucleation surpassed that of atomic hydrogen etching. This greatly shortened the time for incubation. As a result, diamond nucleated on the abundant powders and grew for a longer time, due to a short incubation, so that diamond crystals collided and developed a preferred orientation of the (1 0 0) surface. As mentioned above, the additional evidence supporting the fact that diamond powders were the nucleation sites, is that the sizes of the diamond crystals formed are proportional to the sizes of the diamond powders used.

Finally, it appears that the quality of diamond coatings was not affected by the way that diamond powders were applied to the specimen surface. However, the homogeneity of coatings was affected by how well the diamond powders were dispersed in an aqueous solution. For dip-coating processes, islands of diamond coatings were found on a specimen prepared using Method 8, owing to the poor dispersion of diamond powders in water. For sonication processes, the dispersion of diamond powders was good which resulted in more homogeneous coatings. It is noted that the coating homogeneity was affected by the substrate topology as discussed previously. It is desired, therefore, to have a pore-free, smooth surface in order to obtain continuous, pin-hole-free diamond coatings.

4. Conclusion

Carbon/carbon composite, with a proper surface treatment may be favoured for use as substrate for diamond deposition due to the presence of atomic hydrogen. It is thought that deposition of diamond on CC specimens begins with an incubation period during which diamond nucleation competes with hydrogen etching. It is noted that while atomic hydrogen etches the CC specimen surface, it also generates favoured nucleation sites and therefore leads to the exposure of the edges of prism planes. Under the conditions where no proper pre-treatment is applied, these limited numbers of edges serve as diamond nucleation sites, which can then only yield a poor nucleation density. The nucleation density can, however, be greatly enhanced by introducing high-purity diamond powders on the specimen surface.

These high-purity diamond powders can also greatly suppress the atomic hydrogen etching. Under the present growth conditions, the introduction of diamond powders on a CC specimen surface yields the formation of high-quality diamond with a preferred crystal orientation of (1 0 0) surfaces.

Acknowledgement

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