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Formation of large diamond crystals in oxyacetylene flame chemical vapour deposition

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Diamond coatings were deposited on diamond-polished molybdenum substrates from a premixed oxyacetylene flame for a long time (up to 4 h) at substrate temperatures between 700 and 950 °C, acetylene-to-oxygen ratios 1.02–1.07 and total flow rates between 230 and 310 standard L h^{-1}. The coatings contain, in addition to the densely populated octahedral crystals making a continuous layer of determined thickness, a number of individual large cuboctahedral crystals sticking out far above the layer. A large cuboctahedral crystal is formed from an octahedral one when the latter reaches a certain height at which its temperature becomes sufficiently high for the octahedron-to-cuboctahedron conversion to take place. This conversion was found to occur by a flattening of the octahedron pyramid tip whereby a $\{100\}$ face perpendicular to the growth direction is formed. Both the height of the crystal and size of the $\{100\}$ face increase upon further deposition, reaching up to 230 μm above the octahedral crystals layer and up to about 200 μm, respectively. The large crystals have smooth $\{100\}$ faces, but otherwise often have an irregular shape which may be due to a high temperature favouring deposition of non-diamond carbon.

1. Introduction

Several papers concerning studies of large diamond crystals formed by chemical vapour deposition (CVD) using an oxyacetylene flame [1–3] or a microwave plasma [4] have recently appeared. Snail and Hanssen [1] obtained large (> 100 μm) diamond crystals on non-diamond substrates heated to 900–1000 °C. The crystals often grew from pedestals that thermally isolated them from the substrate, so that their temperature was higher than 1250 °C (the detection limit of the pyrometer used). The crystals had smooth oriented $\{100\}$ faces. Other papers in which this method was used [2, 3] consider procedures directed to preparation of regular large diamond crystals (up to 1 mm). By using microwave plasma, large octahedral crystals were obtained [4].

Some of the questions relevant to large-crystal formation which need explanations are (a) why certain crystals grow more rapidly; (b) why their morphology is changed from an octahedral to a cuboctahedral one; (c) how the crystals are converted from octahedral to cuboctahedral morphology; (d) why the growing faces are oriented perpendicular to the direction of growth. The papers mentioned attempted to explain the majority of these questions, but some of them, (c) and (d) in particular, seem not to have been properly considered. The aim of the present work was to supply evidence contributing to the answers to the above questions.

2. Experimental procedure

The simple apparatus used to deposit diamond has been described previously [5]. A conventional welding torch fitted with a 1 mm welding tip was used. A molybdenum substrate in the form of a plate, polished with a diamond paste, was fixed on a water-cooled copper block. The substrate temperature, (T_s), was regulated by adjusting the thermal contact between the substrate and the copper holder; it was monitored by means of a chromel–alumel thermocouple placed into a hole drilled on the back of the substrate to a depth of approximately 0.5 mm below the substrate surface. Thus, the thermocouple was in the immediate vicinity of the substrate surface heated by the flame. Acetylene and oxygen flow rates and their ratio, R, were controlled by means of flowmeters.

The ranges of experimental conditions used for diamond deposition were total (acetylene plus oxygen) flow rate between 230 and 310 standard L h^{-1}, R between 1.02 and 1.07, T_s from 700 to 765 °C, in one experiment being 950 °C. The deposition time was between 1 and 4 h.

Diamond growth occurred within an approximately circular area on the substrate centred along the flame axis. The region of growth had a diameter of about 5 mm. The coatings often peeled off the substrate and were examined as free-standing samples.

TABLE I Formation of large diamond crystals in combustion-flame CVD

Sample	Deposition time (h)	Substrate temperature (°C)	Total flow rate (Standard L h^{-1})	C_2H_2/O_2 ratio	FWHM of X-ray (111) reflection, 2θ (deg)	Height of main population and largest crystals above substrate surface[a]
1	1	765	310	1.07	0.15	△ at 30–35 μm height □ 8–15 μm higher
2	1	950	265	1.06	0.22	△ at 30–40 μm height, ball-like □ 40–50 μm higher
3	3	735	245	1.02	0.11	△ at 40 μm height □ 40–50 μm higher
4	3	750	270	1.07	0.20	△ at 60 μm height, ball-like □ 160 μm higher
5	4	705	260	1.03	0.14	△ at 50 μm height □ 150–230 μm higher
6	4	725	230	1.02	0.14	△ at 35 μm height □ 45 μm higher

[a] △ refers to the main population of octahedral crystals. □ refers to {1 0 0} faces on the top of largest crystals.

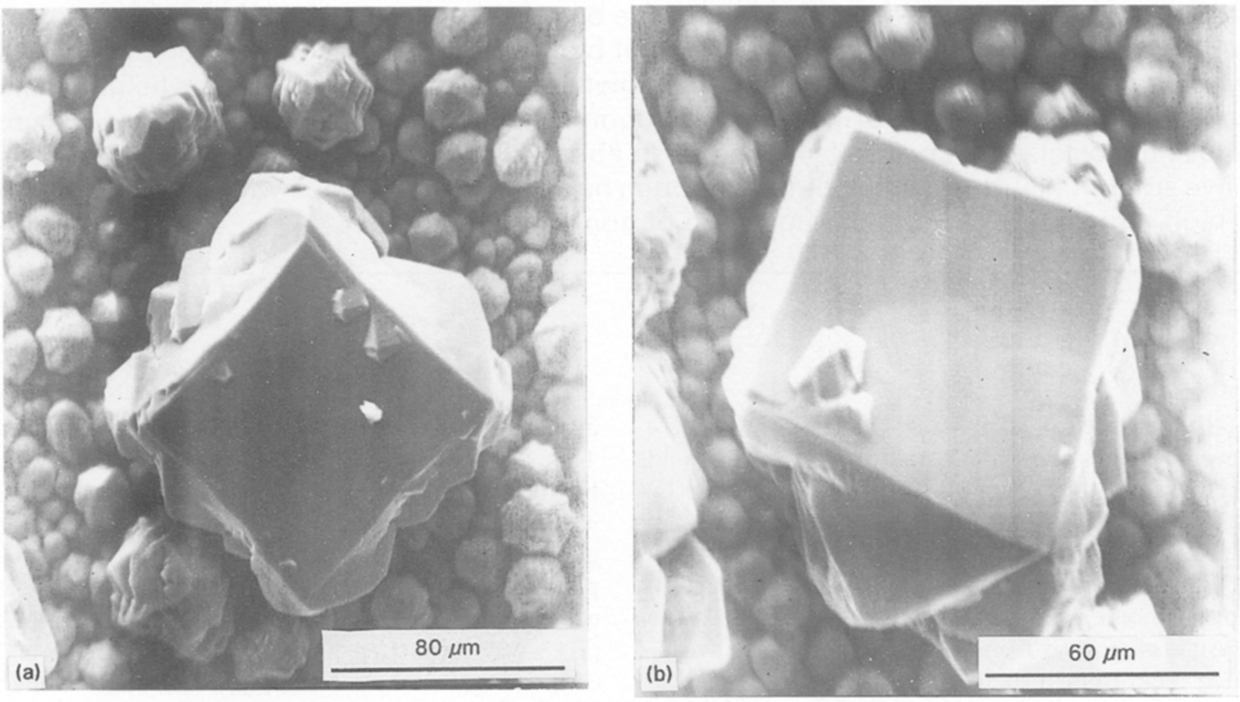


Figure 1 Examples of large crystals in the coatings prepared by 4 h deposition. The large crystals extend considerably above the main crystal population consisting of octahedral crystals.

The diamond coatings were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy.

XRD was used to determine the diamond lattice constant from the (3 1 1) K_{α_1} peak position and full-width-at-half-maximum (FWHM) of the (1 1 1) K_{α_1} profiles corrected for instrumental broadening.

The Raman spectra were obtained using an argon-ion laser, with 514.5 nm line as the excitation wavelength.

3. Results and discussion

When the diamond deposition lasted for 0.5–1 h, incandescent particles appeared. They became more numerous and brighter as the deposition time increased. In the cooled-down coatings grown for 3–4 h, the sparkling particles could be observed by the naked eye. A microscopic study showed that the particles were relatively large cuboctahedral crystals (with size of the {1 0 0} faces up to 200 μm), with the {1 0 0} faces parallel to the plane of the coating (i.e. perpendicular to the growth direction).

Table I shows deposition conditions, and morphology versus height above the substrate surface for typical samples. Fig 1 shows scanning electron micrographs of some samples prepared by 4 h deposition.

The coatings prepared by long deposition times typically consist of densely populated octahedral crystals making a continuous layer of a determined thickness, and individual large crystals sticking out from this layer. It is interesting that the height (thickness) of

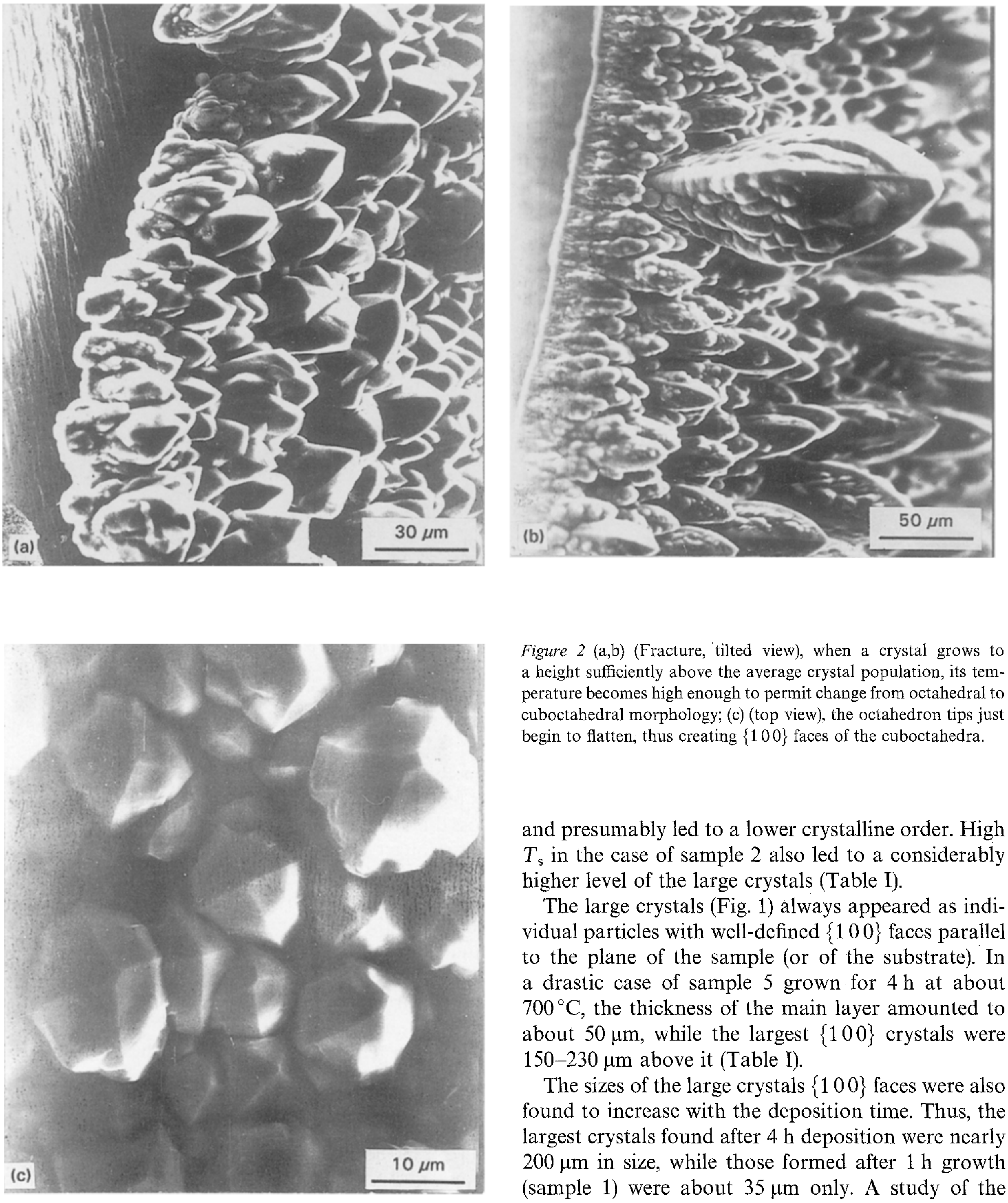


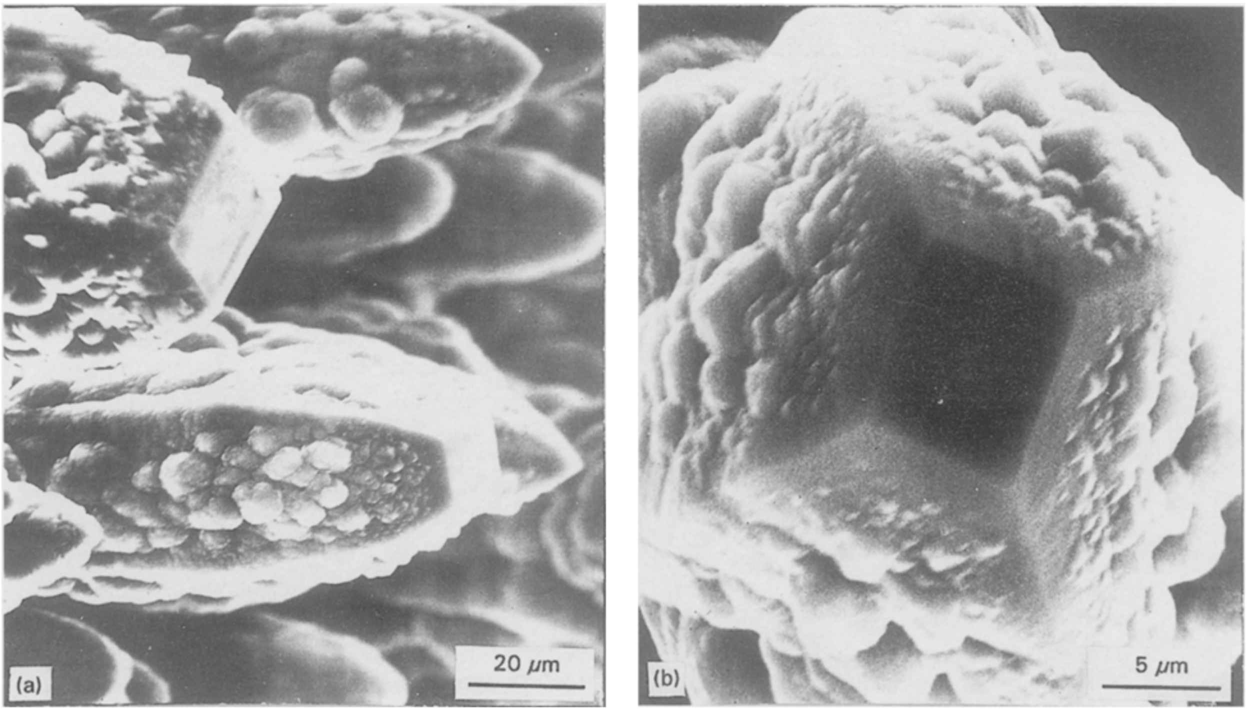
Figure 2 (a,b) (Fracture, tilted view), when a crystal grows to a height sufficiently above the average crystal population, its temperature becomes high enough to permit change from octahedral to cuboctahedral morphology; (c) (top view), the octahedron tips just begin to flatten, thus creating {1 0 0} faces of the cuboctahedra.

the octahedral crystal layer shows little dependence on the deposition conditions, contrary to the size and maximum height of the protruding large crystals (see Table I). The FWHM of the (1 1 1) X-ray reflection has been introduced into Table I as a measure of the crystalline order [5]. The FWHM values depend on the acetylene-to-oxygen ratio, *R*, substrate temperature, T_s, and total flow rate; the lower the *R* value and the higher the flow rate, the lower is the FWHM (and consequently, the higher is the crystalline order). The T_s values are rather close to each other and should not have an important influence on FWHM, except for sample 2, where T_s was considerably higher and presumably led to a lower crystalline order. High T_s in the case of sample 2 also led to a considerably higher level of the large crystals (Table I).

The large crystals (Fig. 1) always appeared as individual particles with well-defined {1 0 0} faces parallel to the plane of the sample (or of the substrate). In a drastic case of sample 5 grown for 4 h at about 700 °C, the thickness of the main layer amounted to about 50 μm, while the largest {1 0 0} crystals were 150–230 μm above it (Table I).

The sizes of the large crystals {1 0 0} faces were also found to increase with the deposition time. Thus, the largest crystals found after 4 h deposition were nearly 200 μm in size, while those formed after 1 h growth (sample 1) were about 35 μm only. A study of the fractured surface shows that large {1 0 0} crystals are formed from the octahedral ones, the tip of the pyramid being converted into a tiny rectangle. This octahedron to cuboctahedron conversion occurs when the crystal is considerably above the main crystal population (Fig. 2).

These phenomena can be explained as follows. During the initial stage of growth certain crystals grow more rapidly. One reason for the different growth rates has been proposed by Wild *et al.* [6] who attempted to explain the often-found phenomenon of preferred orientation. According to Wild *et al.* [6], preferred orientation is a result of the competition of differently oriented crystals during growth, the crystals with their {1 1 0} faces parallel to the substrate surface growing fastest. Given sufficient time, more rapidly growing



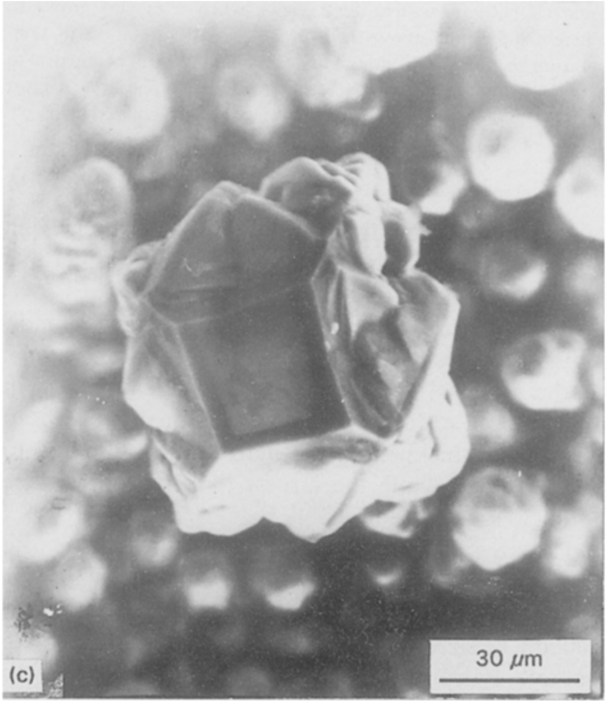


Figure 3 (a) Tilted view of the fractured sample and (b, c) top view of the coating surface showing that large crystals are often irregular, although they have smooth {1 0 0} faces.

crystals will stick out considerably from the mass of average crystals. The protruding crystals receive more heat because their surface area exposed to the flame is larger. On the other hand, such crystals transfer to the substrate almost the same quantity of heat as the average crystals, because they are in contact with the substrate through approximately the same (small) area and their contact with other crystals remains also similar. Therefore, the temperature of the large crystals becomes higher and this, in turn, leads to their higher growth rate, i.e. both temperature and growth rate of the large crystals should increase with time. As the temperature of the large crystals increases, heat loss by radiation becomes significant. The equilibrium is reached at a relatively high temperature when heat loss due to radiation becomes sufficient to compensate for stronger heating. At this point, the large crystals can be considered to be isolated (because their heat loss through the substrate becomes negligible with respect to the heat received from the flame [7]). Snail and Hanssen [1] reported that the temperature of the large isolated crystals was higher than 1250 °C, while the substrate temperature amounted to 900–1000 °C. Cappelli and Paul [7] calculated 1200 °C as the maximum temperature reached by the large isolated crystals.

When the temperature is reached at which the growth rate ratio in the ⟨1 1 1⟩ and ⟨1 0 0⟩ crystal directions becomes sufficiently high, the {1 0 0} faces appear. Although the temperature of the large crystals could not be measured, their blaze shows that it was considerably above 1000 °C.

Fig. 2 shows how the large crystals grow. Fig. 2a and b show the fracture surface of the coating. In Fig. 2a, the main population of the octahedral crystals and the large crystal seen in Fig. 2b has just reached a stage at which its morphology is changed from octahedral to cuboctahedral. Namely, a small flat surface (a {1 0 0} face) can be observed on the tip of the crystal. This can also be seen in Fig. 2c, showing that octahedral pyramid tips of some crystals have just begun to flatten.

A further stage of growth of the {1 0 0} faces can be seen in Fig. 3, both on the fracture (Fig. 3a) and top view (Fig. 3b,c). From the scanning electron micrographs it can also be seen that, although the {1 0 0} faces are smooth, the growth conditions are not always suitable for well-defined cuboctahedral crystals. Irregularities appear, such as droplet-like formations on the rim of the growing crystals, Fig. 3a.

The reason for the irregular growth of the large crystals may be an easily induced disturbance in heat and species transport through a thin boundary layer at the substrate (with thickness ~100 μm [8] or even less because of the high gas velocity [9]), because of comparable sizes of the boundary layer and the large crystals [2]. In a study of the effects of the boundary-layer thickness [2] in which the large crystal growth in the hot-filament CVD (with a boundary layer 5–10 mm thick) was compared with that in a combustion flame, the authors conclude that, unlike in the combustion flame, in the hot-filament method the crystals grow steadily and epitaxially in a layer-by-layer growth mode. In our case, where the linear velocity of the gas mixture is close to turbulent flame conditions [10], the disturbance of the boundary layer should be more pronounced. On the other hand, such conditions have been found to result in higher crystal perfection [11], because of an increased diffusion of etchant species from the ambient air at high gas velocities. Another reason for the irregular growth of the large crystals may be their high temperature which may favour deposition of a non-diamond carbon.

A study of the coatings containing large crystals by X-ray diffraction showed that their lattice constants covered a narrow range between 0.3564 and 0.3566 nm. The FWHM values (Table I), found to be the best indicator of crystalline order [5], cover the range from 0.11° to 0.22° 2Θ, the highest value (corresponding to the lowest crystalline order) being found for sample 2 deposited at the highest T_s from the flame rich in acetylene (high R value). The lowest FWHM (the highest crystalline order) was found for sample 3 with the lowest R value. However, because the X-ray beam covers the entire volume of the sample, this method does not permit the large crystals to be studied separately.

The Raman spectra taken for some of the samples show, in addition to the diamond line in the vicinity of $1332\,\mathrm{cm}^{-1}$, the band at $1520–1550\,\mathrm{cm}^{-1}$ due to graphitic carbon. The spectra were taken from areas both relatively abundant in large crystals and without them. No significant differences were found either in the Raman diamond line position and width, or in the presence of the band at $1520–1550\,\mathrm{cm}^{-1}$. However, no definite conclusion can be derived from the results obtained, because none of the spectra can be considered to represent the large crystals alone.

4. Conclusion

During the relatively long-term deposition of the diamond coatings, some crystals grow more rapidly, sticking out from the mass of average crystals. Such crystals receive a larger quantity of heat from the flame because their surface exposed to the flame is larger. Their heat loss through the substrate surface remains virtually unchanged, so that their temperature increases and this, in turn, leads to the more rapid growth. This continues until a temperature is reached at which heat loss by radiation compensates for the larger heating. The result is the formation of crystals that are far above the average crystal population. At some stage of their growth, i.e. when they reach a sufficiently high temperature, the large crystals change their morphology. This occurs by flattening of the octahedral pyramid tips which become tiny rectangles ($\{100\}$ faces) parallel to the plane of the coating, thus converting the octahedral crystals to cuboctahedral ones. The newly formed $\{100\}$ faces grow by further deposition, reaching up to 200 μm after 4 h. The large crystals have smooth $\{100\}$ faces, but otherwise often have an irregular shape due to the high temperature favouring deposition of non-diamond carbon.

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