

SOME PHENOMENA AND ANALYSES IN GROWING DIAMOND

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Some peculiarities in the process for the production of synthetic diamonds from graphite disks, by the static pressure catalyst method, have been studied in detail. Results from various analytical methods applied to the diamonds grown have confirmed that the chemical constituents of all media in contact with diamond, i.e. the medium for transmitting pressure, the graphite and the catalyst alloy, can be incorporated into the growing diamond crystals. They usually segregate along the {110} planes. Some pyrophyllite grains can be seen in the cross section of the synthetic diamond disks. Many grains of the diamond are buried in some larger grains of pyrophyllite with only one crystal face of the diamond being visible. Some diamond grains are completely covered by pyrophyllite. It could be deduced that during melting pyrophyllite can function as the transporting medium for carbon to accelerate the transformation of the electronic state of carbon from SP^2 into SP^3 .

1. Introduction

Synthetic diamond can be made by a variety of methods, but the static pressure catalyst method is most often used in industry. The main feature is that graphite is the source of carbon and the transformation is accomplished by means of a molten catalyst under high pressure and temperature. Because of the growth conditions various kinds of impurities are usually incorporated into the synthetic diamonds.

A medium for transmitting pressure must be used along with the source of carbon and the catalyst. In general, it has four functions: transmitting pressure, supporting the reaction cylinder, retaining heat and insulating. On the functions beyond those mentioned above, little has been published so far. In fact, it has been found in particular that pyrophyllite near the reaction chamber can be transformed into new pyrophyllite polymorphs under high pressure and temperature. By using the word "pyrophyllite" in the following sections we mean pyrophyllite and its polymorphs.

2. Experimental

The diamond was made by the static pressure catalyst method. The experiment was performed

using a reaction chamber containing graphite and the metal catalyst. The graphite disks and the catalyst disks were alternately piled up to form the reaction cylinder and the ends of which were capped by two steel bowls having a pyrophyllite core. Subsequently, the bowls and the reaction cylinder were fitted into the centre of a cube made of the medium for transmitting pressure. Then the cube was placed into a cubic press and subjected to a high pressure. An electric current was passed through the reaction chamber, which melted the metal catalyst and caused some of the graphite to undergo transition to diamond. Thereafter the sample was cooled and the pressure released. One cycle took about 8 min. The pressure and the temperature during diamond synthesis were about 5.5 GPa and 1400°C, respectively. The catalyst used was $Ni_{70}Mn_{25}Co_5$ and the graphite used was T64P. The bulk cube acting as the medium for transmitting pressure was formed with pyrophyllite powder.

After the experiment, the reaction cylinder was set free by breaking the reaction chamber. The graphite was removed by dissolving in dilute $H_2SO_4 + HNO_3$. After removal of graphite it became evident that many diamond grains and a few pyrophyllite grains were buried in the catalyst disks (fig. 1).

The catalyst was then dissolved in dilute HNO_3 .



Fig. 1. Layer with synthesized diamonds after removal of graphite by chemical treatment. The white region indicated by the arrow on the top photograph is pyrophyllite, the grains on the bottom photograph are diamond. Magnification $15\times$.

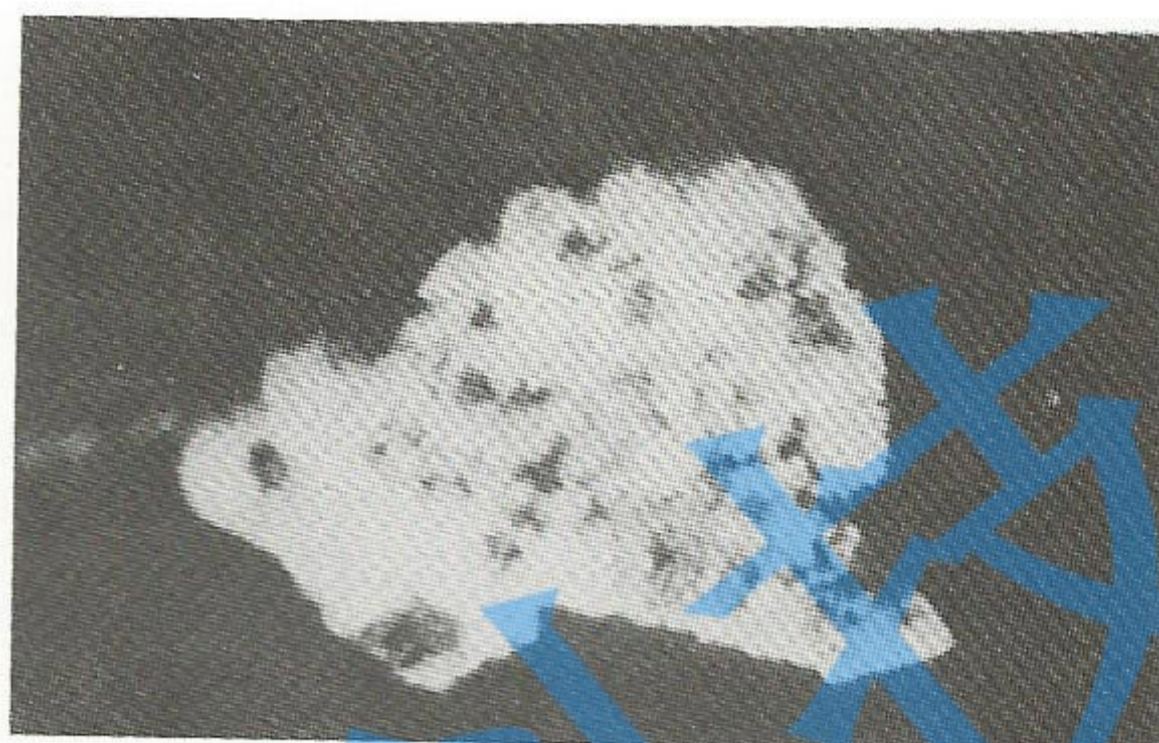


Fig. 2. A bulk of pyrophyllite with many diamond crystals. Magnification $15\times$.

The following interesting phenomena were observed: Some diamond grains were buried in a larger grain of pyrophyllite (fig. 2) which occasionally covered the diamond grains completely.

Some surfaces of the pyrophyllite in contact with diamond crystals were smooth and dense (fig. 3a), others showed a network structure (fig. 3b). For convenient comparison, fig. 3c shows the common metal film in contact with diamond. Some grains of pyrophyllite approached quite regular

spherical forms (fig. 4). The surface of these grains appeared very smooth even at high magnifications (about $10,000\times$).

It is conceivable from fig. 3b that pyrophyllite and the catalyst had perhaps been penetrating each other under the conditions for growing diamond. After the catalyst was removed by dilute HNO_3 , the pyrophyllite residue exhibited a network structure. It was confirmed by the pyrophyllite grains approaching quite regular spherical forms (fig. 4) that the pyrophyllite was perhaps molten under the condition for growing diamond.

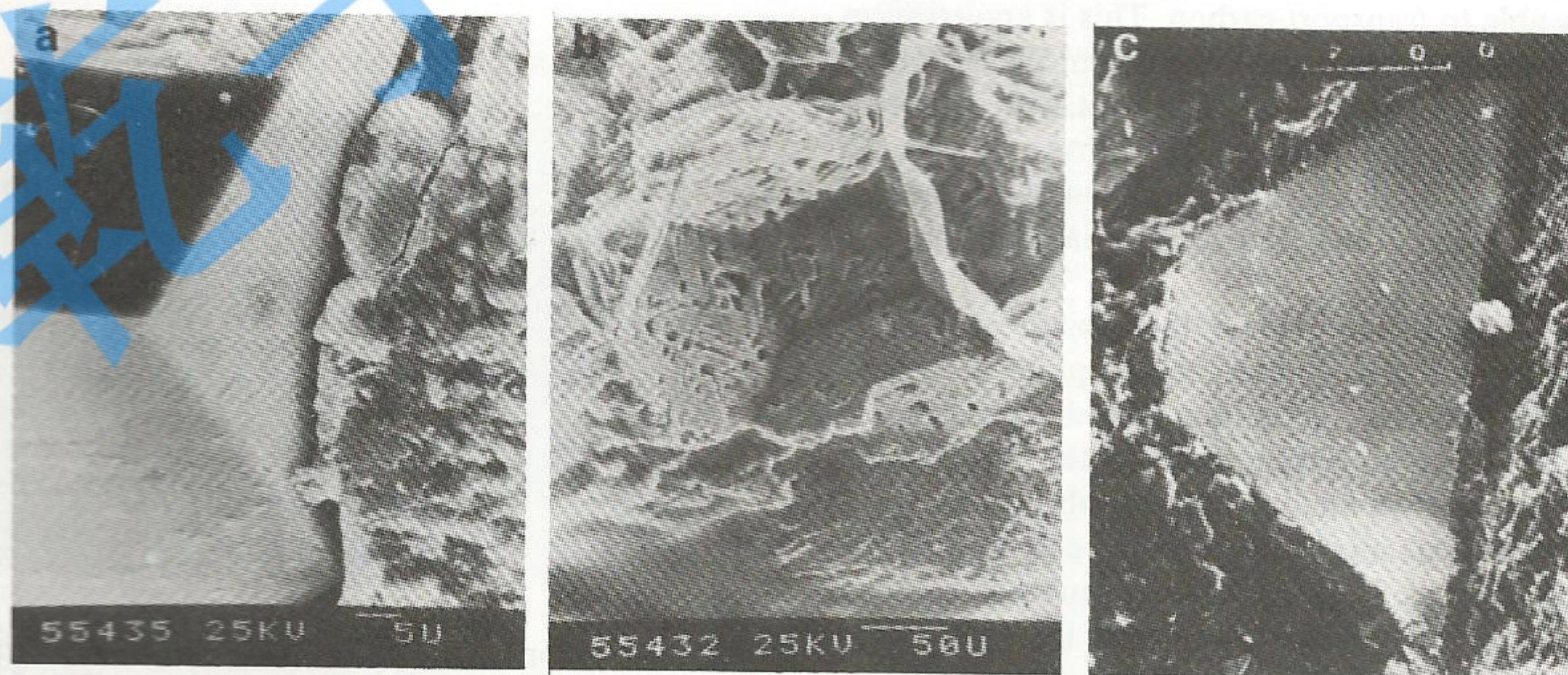


Fig. 3. Scanning electron micrograph with the negative form of a diamond crystal. (a) The surface of the pyrophyllite is smooth and dense. (b) The surface of the pyrophyllite showing a network structure. (c) The metal film in the catalyst disk.

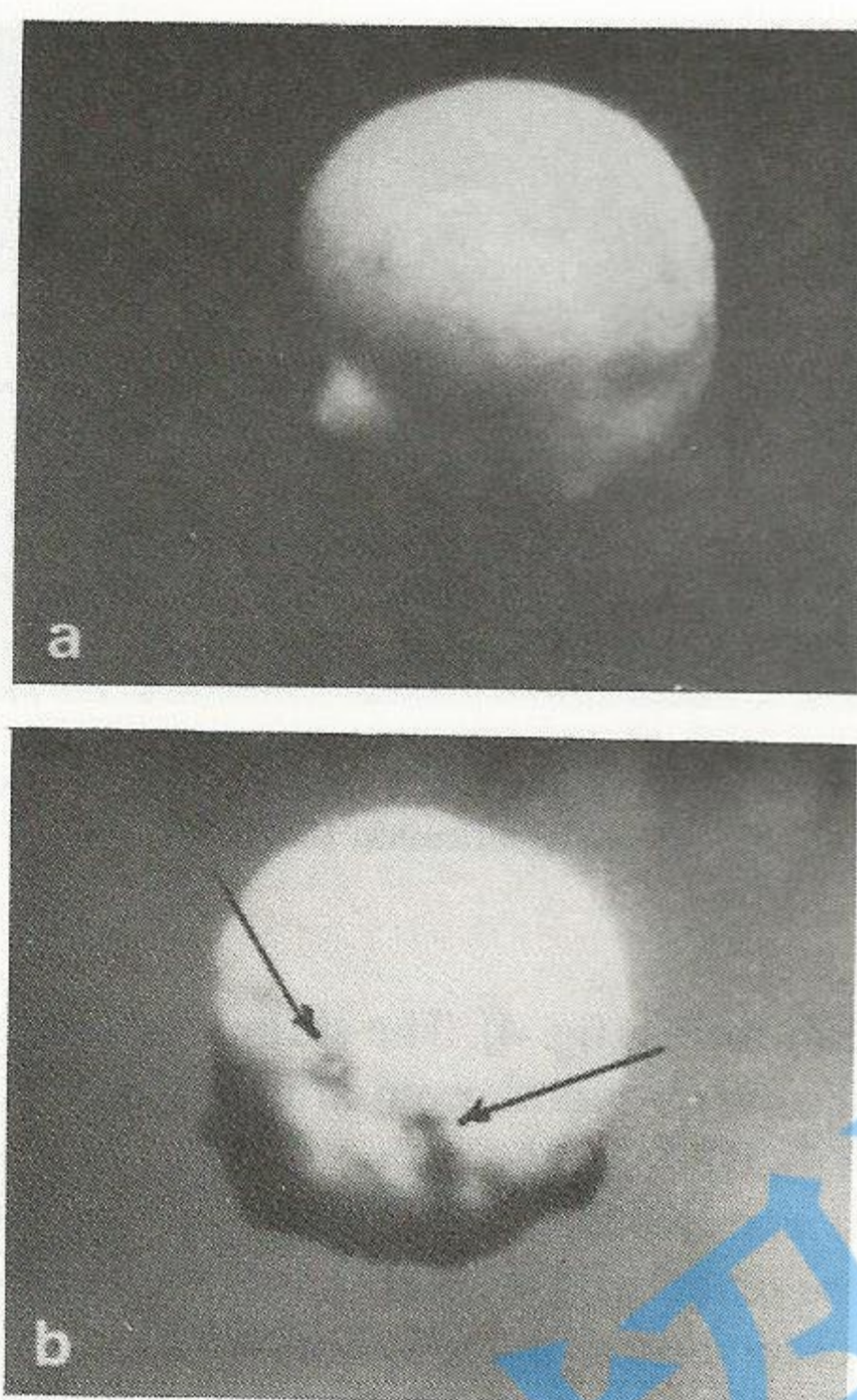


Fig. 4. The molten pyrophyllite approaching quite regular spherical forms. (a) The surface is very smooth. (b) Two diamond crystals can be discerned. Magnification $15\times$.

Where pyrophyllite and the catalyst did not penetrate each other, molten pyrophyllite was perhaps able to transport carbon. This is argued from fig. 3a. For convenient comparison, fig. 3c shows the common metal film in contact with diamond which is equally as smooth and dense as fig. 3a. So the growth of diamond crystals on two kinds of substrates could have proceeded via similar mechanisms.

In order to understand the growth process of the diamond, the catalyst, the graphite, the pyrophyllite, the disks containing the diamond grains and the diamond were investigated by spectral semiquantitative analysis, atomic absorption analysis, chemical analysis, scanning electron microscope analysis, X-ray diffraction analysis and ion micro-analysis. Tables 1-3 show the results obtained.

Most chemical constituents in the medium for transmitting pressure and in the graphite were

found in the synthesized catalyst disks; for example, the aluminium and silicon concentration exceeded 3% by weight in the non-pyrophyllite portions of the disks (table 2). Moreover, most chemical constituents in the catalyst, the pyrophyllite, and the graphite were found in the synthetic diamonds. Various atoms dissolved in the catalyst can bond with carbon atoms on the surface of the growing diamond by chemical adsorption. Aluminium and silicon appeared to be incorporated in the diamond more easily than nickel, manganese and cobalt when the growth rate of the crystal was low, i.e. when the linear growth rate was less than $0.4\ \mu\text{m/s}$ (table 1). Nickel, manganese and cobalt were easily incorporated in the diamond when the growth rate of the crystal was high, e.g. when the linear growth rate was more than $1\ \mu\text{m/s}$, because a large quantity of mother solution was included (table 1). Some of the inclusions were formed by clustering of the pertinent impurities. The inclusions usually segregated along the $\{110\}$ planes (fig. 5). The surface of the diamonds growing on the pyrophyllite had a higher concentration of impurities than those of the other diamonds (table 3), especially sodium, aluminium, silicon, potassium, titanium, manganese, and iron.

The sensitivity of the various analytical methods for the same element was different and the sensitivity of the various elements by the same

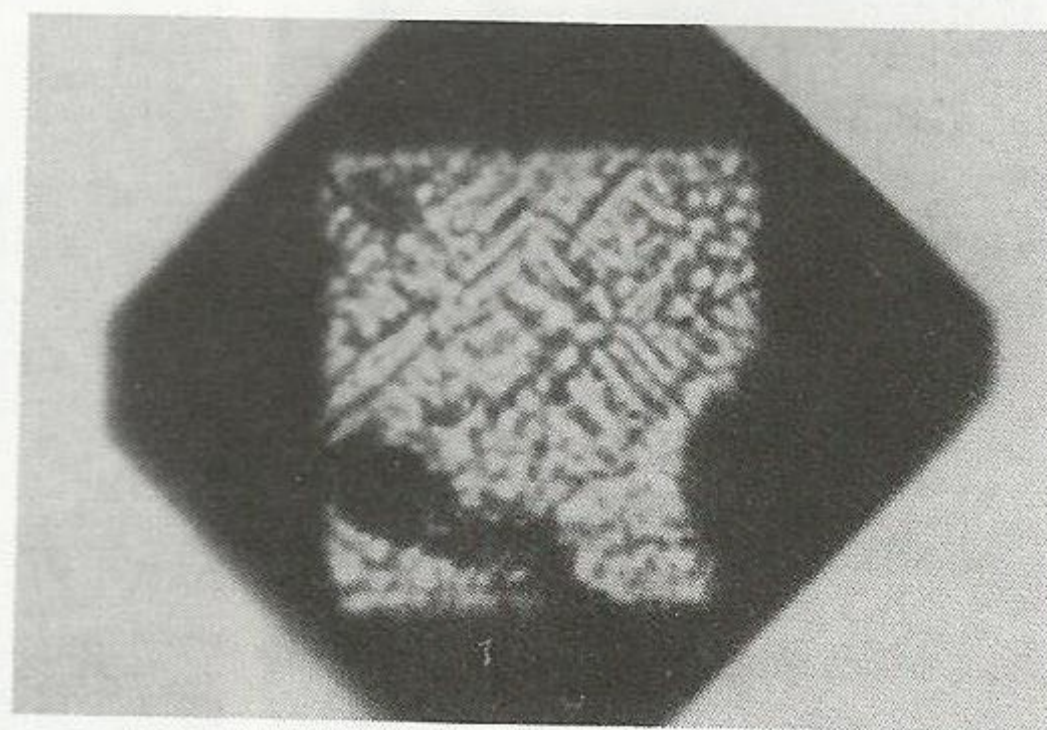


Fig. 5. Photograph of a cubo-octahedral diamond. The bright square region is the (100) face. Black triangles are $\{111\}$ faces. The inclusions segregate along the $\{110\}$ planes. Magnification $24\times$.

Table 1
Element contents (wt%)

Elements	Synthetic diamonds			Pyrophyllite	Catalyst used
	No. 1	No. 2	No. 3		
Ni	1.26 ^{a)}	0.06	0.002	0.003	(70)
Mn	1	0.2	0.01	0.0077 ^{b)}	(25)
Co	0.95 ^{a)}	0.006	0.003	< 0.001	(5)
Fe	0.19 ^{a)}	0.03	< 0.003	0.74 ^{b)}	0.0405 ^{a)}
Ca	1	0.1	0.06	0.29 ^{b)}	
Cu	0.01	0.002	0.0001	< 0.001	0.0144 ^{a)}
Zn	0.01	0.01	—	—	0.0029 ^{a)}
Cr	0.01	—	—	0.012	
Ti	0.003	0.0025	0.001	1.2 ^{b)}	
Mg	0.01	< 0.01	≪ 0.01	0.06 ^{b)}	
K	~ 0.2 ^{a)}	—	—	0.49 ^{b)}	
Si	0.08	0.4	0.025	24.45 ^{b)}	
Al	0.1	0.3	< 0.01	20.25 ^{b)}	
Na	0.01	0.2	< 0.01	0.82 ^{b)}	
B	0.003	0.15	0.005	0.004	

^{a)} Results determined by atomic absorption analysis.

^{b)} Results determined by chemical analysis.

The other figures are results determined by spectral semiquantitative analysis.

The synthetic diamonds are classified by their ferromagnetism. No. 1, ferromagnetism, was the strongest; No. 3 the weakest. The linear growth rate of most No. 1 diamond was more than 1 $\mu\text{m/s}$, of No. 3 less than 0.4 $\mu\text{m/s}$ and of No. 2 intermediate.

analytical method was also different. So this difference ought to be considered when using tables 1-3.

3. Analyses

The nature of chemical adsorption is bonding on the interface, hence it has selectivity. It is well

Table 2
Element contents in the catalyst after synthesis by scanning electron microscope analysis

Elements	Content (wt%)
Na	8.24
Mg	4.73
Al	3.40
Si	3.37
Cl	1.38
Ca	0.22
Ti	0.04
Mn	20.35
Fe	1.48
Co	4.46
Ni	52.33

known that the smaller the value of the heat of formation of a new compound, the easier the compound is to form. According to this thermodynamic principle, one of the impurities most likely

Table 3
Height of the main peaks of the elements by ion microanalysis

Nuclei	Diamond growing on pyrophyllite	Diamond not growing on pyrophyllite
¹ H	1.89	0.62
⁷ Li	0.04	0.00
¹³ C	1.00	1.00
¹⁴ N	0.55	0.51
¹⁶ O	1.12	0.22
²³ Na	1.26	0.07
²⁶ Mg	0.19	0.13
²⁷ Al	4.47	0.19
²⁹ Si	0.94	0.01
⁴⁰ Ca	1.47	0.43
⁴¹ K	0.87	0.01
⁴⁸ Ti	0.62	0.01
⁵² Cr	0.15	0.03
⁵⁵ Mn	5.53	0.16
⁵⁶ Fe	0.81	0.05
⁵⁸ Ni	0.04	0.03

to be incorporated into the growing diamond is titanium followed by chromium, aluminium, silicon, calcium, molybdenum, iron, cobalt and nickel in descending order [1]. Of course, the concentration of impurity elements in diamond also depends on their amount around the growing diamond.

If the melting pyrophyllite penetrated between the graphite layers, it could possibly enclose the diamond crystals already grown. But this process appears rather unlikely, at least for the larger diamond crystals because the thickness of the catalyst disks was only 0.5 mm.

It was deduced from the observed spherical grains that a small portion of pyrophyllite had melted during diamond synthesis. Pyrophyllite is a phyllosilicate mineral. Its basic structural unit is the silicon-oxygen tetrahedron. The silicon-oxygen bond length is about 1.62 Å. It has been pointed out in many investigations that silicon in the center of the tetrahedron can be substituted by aluminium in nature [2]. One can imagine that silicon can also be substituted by carbon in the pyrophyllite within the reaction chamber.

It is well known that a melting silicate can be regarded as an ionic liquid through which the carbon atom can easily diffuse. The carbon atom could occupy the center of the silicon-oxygen tetrahedron; this is facilitated because of the various defects usually present in the pyrophyllite. Furthermore, the strength of the O-C chemical bond is 1076.5 kJ/mol and exceeds that for the O-Si bond at 787.7 kJ/mol, i.e. when the carbon atom substitutes the silicon atoms in the silicon-oxygen tetrahedra, the system should gain thermodynamic stability.

4. Conclusions

Most chemical constituents in the medium for transmitting pressure, the graphite, and the cata-

lyst alloy can be incorporated into the growing diamond. The driving force for the impurities to be incorporated into growing diamond is chemical adsorption when the growth rate of the crystal is low. There is evidence that aluminium and silicon are incorporated into diamond more easily than nickel, manganese, and cobalt.

The inclusions are usually formed by clustering of the impurities incorporated into the diamond, and the inclusions usually segregate along {110} planes.

The pyrophyllite can penetrate into the reaction chamber. Hence the pyrophyllite can take part directly in the growth process of diamond. It has been confirmed that melting phenomena of pyrophyllite can play a role for nucleation and growth of diamond.

Some portions of pyrophyllite in the reaction chamber can act as the substrate on which a few diamond crystals can nucleate and gradually grow. It could be deduced that the melting pyrophyllite can function as a transporting medium for carbon helping to accelerate transformation of the electronic state of carbon from SP^2 into SP^3 . Carbon might also substitute for silicon in the silicon-oxygen tetrahedra of the pyrophyllite structure. Therefore pyrophyllite can be beneficial in nucleating and growing of diamond.

References

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