JOURNAL OF MATERIALS SCIENCE 32 (1997) 4309–4318

High-pressure synthesis of diamond from phenolic resin

AKIFUMI ONODERA, KATSUTOMO TERASHIMA*, TAKESHI URUSHIHARA‡, KAICHI SUITO
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan
HITOSHI SUMIYA, SHUICHI SATOH
Itami Research Laboratory, Sumitomo Electric Co., Itami, Hyogo 664, Japan

Two kinds of phenolic resin, novolak and resols, have been studied with an addition of cobalt at pressures between 2 and 4 GPa and at temperatures from 1300 to 1900 °C, all under thermodynamically graphite-stable conditions. Diamond was synthesized from these resins which had been pre-fired at 500–1000 °C. From such resins, carbon precursors carrying a great number of radicals, being nearly free of hydrogen and oxygen, and turbostratic in structure, can be constructed. The pressure–temperature conditions suitable for the diamond synthesis were dependent on the pre-firing temperatures. The cobalt served as a catalyst–solvent, similar to the case of conventional diamond synthesis from graphite under diamond-stable conditions. Well-defined single crystals cubo-octahedral in shape, measuring 0.3–0.7 mm across and classified as type Ib were obtained.

1. Introduction

Diamond is an everlasting material because of its beauty and extreme hardness. It is currently used in industrial applications owing to, besides the hardness, the very high thermal conductivity. Synthesis of diamond has been performed with various methods over a wide range of pressures from about 10^2 to 10^{10} Pa [1]. The methods can be categorized basically into two groups in terms of the pressure regime. Low-pressure diamond synthesis proceeds via deposition from gaseous hydrocarbons at conditions where graphite is thermodynamically stable. The synthesis of diamond at high pressures is carried out within the diamond-stable field, and diamond is formed either through precipitation from molten carbon–metal eutectics or through solid-state conversion directly from graphite.

In addition, there is another category in the high-pressure diamond synthesis: a study performed in the graphite-stable region on the carbon phase diagram. Niedbalska and co-workers [2–4] succeeded in synthesizing diamond at a pressure of 3.8 GPa and at temperatures between 1700 and 2000 °C using phenolic resin as the starting material. The formation of diamond was strongly governed by the temperature for firing the resin before subjecting it to a high pressure and a high temperature. Little explanation was given of the characteristics of the fired sample, however. From a similar experiment undertaken at 3.1 GPa and 1200 °C, Brannon and McCollum [5] also obtained diamond.

Because this subject area is intermediate between the low- and high-pressure regimes and yet has been quite unexplored, it is of great importance to characterize the phenolic resin better, to determine the mechanism of the diamond formation, and further to investigate the synthesized diamonds. While, in the preceding studies, only one kind of phenolic resin was dealt with [5] or, otherwise, the resin was unspecified [2–4], we have studied two kinds of phenolic resin, novolak and resols, in order to study any difference or similarity between them. The resins were pre-fired at several different temperatures up to 1000 °C and, after the physical as well as chemical changes caused by the pre-firing were studied, subjected to various pressure–temperature conditions in the graphite-stable region, as opposed to each single pressure condition studied in the previous work [2–5]. The use of phenolic resin, at the same time, relates to our continuing studies on diamond synthesis from carbonaceous materials other than graphite [6–10].

2. Experimental procedure

2.1. Phenolic resin

Novolak and resols supplied by Sumitomo Dures Co. were studied. The two resins differ in the catalysts used for preparing them from phenol and formaldehyde: tartaric acid for the novolak and NaOH for the resols. They were fired at various temperatures up to 1000 °C for 2 h in N_2 (99.99% pure) gas. As a result of the firing the resins were decomposed and carbonized. The

---

*Present address: Komatsu Co., Hiratsuka, Kanagawa 254, Japan.
‡Present address: Japan Railway-West Co., Kita, Osaka 530, Japan.

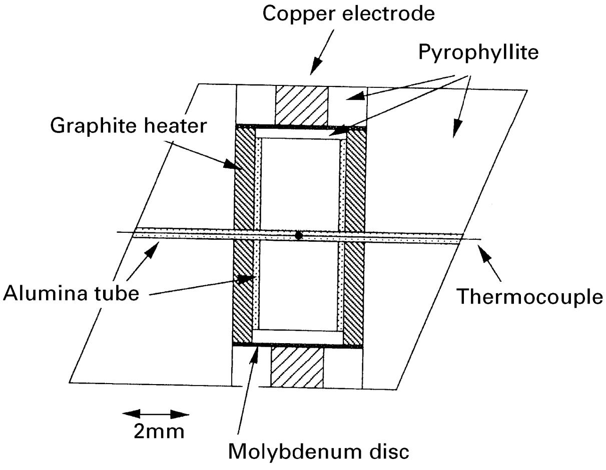


Figure 1 Cross-sectional view of an octahedral cell assembly.

extent of carbonization was estimated from X-ray diffraction, infrared absorption, electron spin resonance (ESR) and electrical resistance measurements. Elemental analysis was also undertaken.

2.2. High-pressure technique

Each fired resin was mixed with cobalt in a ratio 7 : 12 by weight and was pressurized by a high-pressure apparatus of octahedral anvil type [11]. Fig. 1 shows an assemblage of an octahedral sample cell made of pyrophyllite. The sample to be studied was encapsuled in an alumina tube which in turn was placed inside a graphite heater. A high temperature was attained by passing an alternating current through the heater. The temperature was monitored with a Pt–(Pt–13% Rh) thermocouple inserted at the centre of the cell. No correction was made to the effect of pressure on the electromotive force. The pressure applied to the sample was estimated from a load–pressure relation obtained from separate experiments, employing Bi as a calibrant [12].

After duration of high temperature for 20 min while the pressure was kept constant, the sample was rapidly cooled to room temperature. The pressure was then released to retrieve the sample. All the retrieved samples were subjected to X-ray diffraction and optical microscopy observation. Some were washed with aqua regia and with hot chromic acid mixture. The residue was analysed by Raman scattering, visible absorption, infrared absorption, optical microscopy and interferometric microscopy.

3. Results

3.1. Characterization of the phenolic resin

Fig. 2 shows the X-ray diffraction patterns of the resols fired at various temperatures prior to the high-pressure treatment. The diffraction patterns of the resols pre-fired at temperatures below 500 °C show a single halo at about 20°, being essentially similar to that of unfired sample. At 700 °C there occurs a conspicuous change in the pattern as envisaged by shift of the halo from about 20 to26° and by appearance of the (10) band at approximately 43°. These are suggestive of the development of hexagonal network layers stacked roughly parallel to each other. The samples are actually approaching graphite but, even at 1000 °C, remain turbostratic [1] and the layers are rotationally disordered.

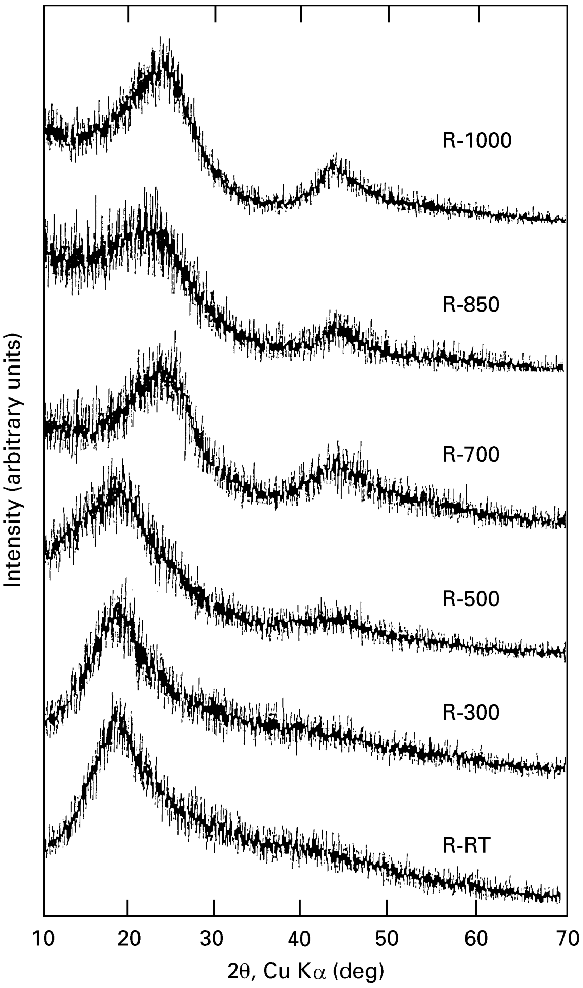


Figure 2 X-ray diffraction patterns of the resols taken prior to the high-pressure treatment. R denotes the resols and the numbers represent the pre-fired temperatures. R-RT is the unfired sample.

Infrared absorption spectra of the resols are shown in Fig. 3. Absorptions assigned to O–H stretching vibration (band a; see [13] for the assignment henceforth), aromatic and aliphatic stretching vibrations (bands b), carbonyl group (bands c), aromatic rings (bands d and e), aliphatic deformation vibrations (bands f and g), C–O stretching and O–H deformation vibrations (bands h, i and j), aliphatic ether (bands l) and aromatic C–H out-of-plane vibrations (bands q and r) are all observable up to 300 °C. A weak unassigned band s disappears at 300 °C. At 500 °C, there appears a band (band v) that is responsible for quinone and unassigned bands u, w and x. Instead band e and some other unassigned bands (n, o and t) disappear. Also, bands a, c, g and l are very much weaker. Above 700 °C, no absorption is discernible in the spectra. These changes show that the resin exhibits a marked chemical transformation between 500 and 700 °C.

Fig. 4 shows typical examples of ESR spectra for the unfired and fired resols. From such spectra, the

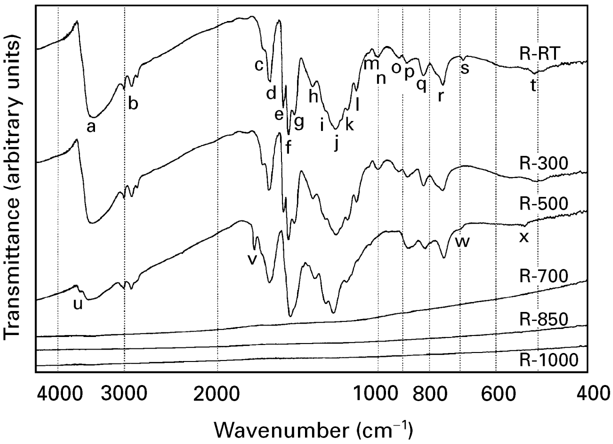


Figure 3 Infrared absorption spectra of the resols taken prior to the high-pressure treatment. The abbreviations are the same as in Fig. 2. The spectra were recorded with an infrared spectrometer (Shimadzu FTIR-8100) for pellets of the samples mixed with KBr.

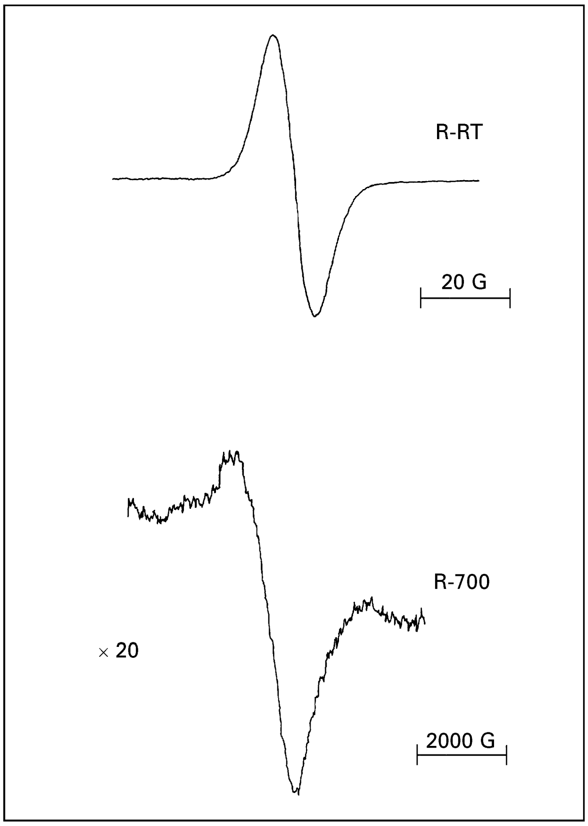


Figure 4 ESR spectra of the resols taken with a JEOL JES-ME-2X. The abbreviations are the same as in Fig. 2.

g value, spin density, full width at half-maximum (FWHM) and antisymmetric parameter, A/B, can be derived as shown in Table I. For every parameter in Table I, a substantial change takes place between 500 and 700 °C. The increase in the spin density in this temperature range is ascribable to free radicals developed by decomposition of the phenolic resin. We note that there appear maxima in the spin density and FWHM at 500 °C for the novolak and at 700 °C for the resols. The decrease in the spin density at higher temperatures can be interpreted by recombination of free radicals and subsequent approach to graphite [14, 15].

TABLE I Parameters in the ESR spectra of the phenolic resins

	Fired temperature (°C)	g	Spin density[a]	FWHM[a]	A/B[a]
Novolak	Unfired	2.004	1	1	1
	300	2.003	1	1	1
	500	2.002	10^2	10^2	1
	700	2.001	10	10	1.5
Resols	Unfired	2.004	1	1	1
	300	2.004	1	1	1
	500	2.003	10	1	1
	700		10^4	10^2	
	850		10	10	

[a] Relative to the value of the unfired sample.

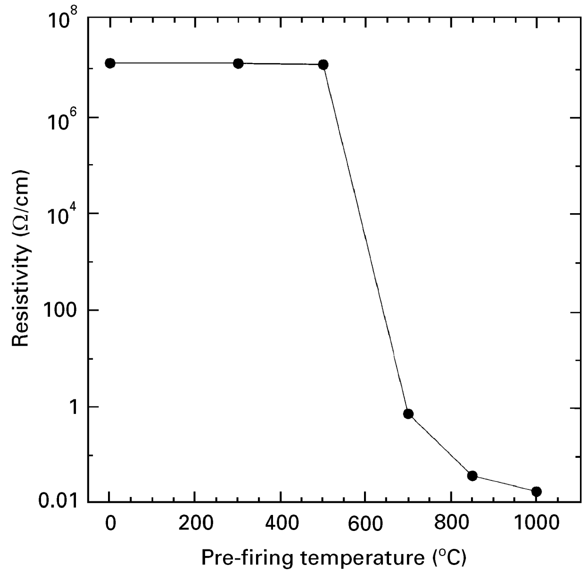


Figure 5 Room-temperature electrical resistivity of the resols against pre-firing temperature. The measurements were undertaken at 6 GPa.

Fig. 5 shows the electrical resistivity of the resols as a function of fired temperature. The resistivity was measured at room temperature with either the two- or the four-probe method, depending on the resistivity range. For each measurement, a pressure of 6 GPa was applied to the sample in order to eliminate any contact resistance. The resistivity exhibits a remarkable drop on firing the sample to 500 °C. Firing above 700 °C causes little further decrease in the resistivity.

Table II shows results from elemental analysis on the novolak and resols. Atomic concentrations of hydrogen and oxygen with respect to carbon, derived from Table II, are shown in Fig. 6. Decreases in the amount of both hydrogen and oxygen take place above 300 °C in the two resins. In detail, the decrease in the hydrogen content begins at 300 °C while a decrease in the oxygen content can be seen at 500 °C. The decreases continue to approximately 700 °C in the two resins and, in the novolak become essentially unaltered at higher temperatures.

From the fact that the changes shown above agree with each other, a process of the carbonization occurring within the phenolic resins can be viewed as

TABLE II Elemental analysis for the phenolic resins (averaged amount from two independent measurements)

	Fired temperature	Averaged amount (wt%)			
		C	H	N	O
Novolak	Unfired	76.00	5.57	1.36	12.28
	300	75.98	5.47	0.20	13.49
	500	80.84	4.65	< 0.1	9.69
	700	91.29	1.19	< 0.1	3.69
	850	92.29	1.14	< 0.01	1.18
	1000	93.00	0.82	< 0.01	1.12
Resols	Unfired	74.45	5.74	< 0.1	14.40
	300	75.22	5.58	< 0.1	13.78
	500	81.38	4.36	< 0.1	9.25
	700	84.64	1.41	< 0.1	7.74
	850	87.56	0.68	< 0.1	6.88
	1000	88.45	0.35	0.37	4.84

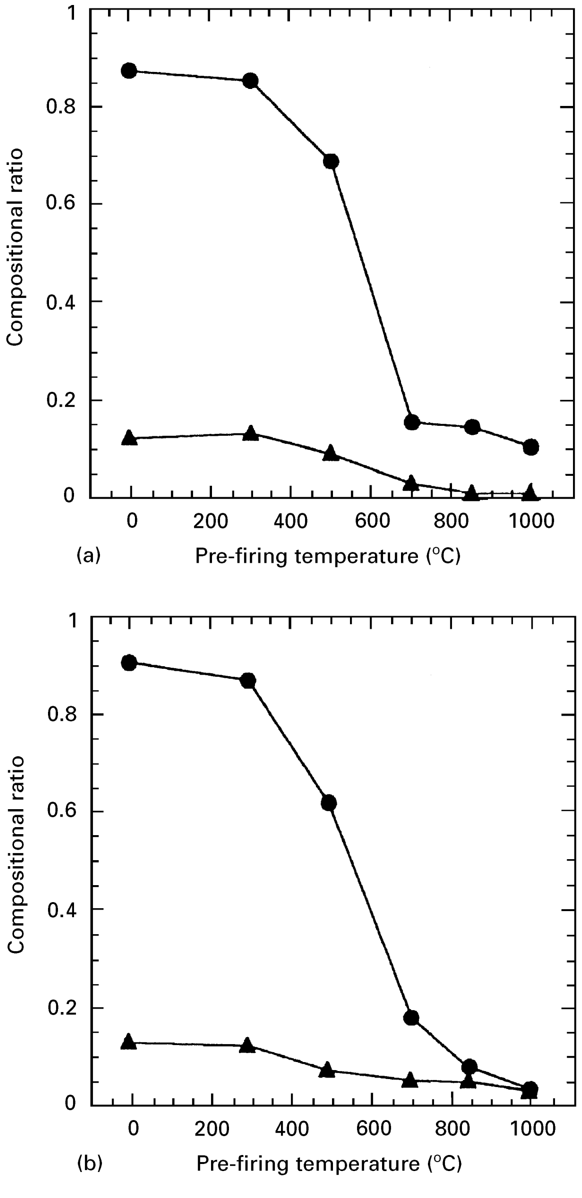


Figure 6 Atomic concentrations of hydrogen (●) and oxygen (▲) relative to carbon as functions of pre-firing temperature for (a) the novolak and (b) the resols.

follows. The resins begin to decompose beyond 300 °C, yielding radicals, breaking carbon–hydroxyl bonds and instead generating carbon–oxygen double bonds. The decomposition becomes drastic between 500 and 700 °C. At temperatures between 700 and 850 °C, the radicals start to recombine and, consequently, condensation takes place among benzene rings to form layers consisting of hexagonal networks. Such layers are stacked roughly parallel to each other but, even at 1000 °C, they are rotationally disordered. The samples are turbostratic and hence are good carbon precursors [1].

3.2. High-pressure treatment

Pressure–temperature conditions and the phases obtained from the novolak and resols are respectively shown in Figs 7 and 8. Pressures between 2 and 4 GPa and temperatures from 1300 to 1900 °C have been studied. In each diagram we show the diamond–graphite equilibrium line [16] and the melting line of cobalt [17]*. Some important points can be derived from Figs 7 and 8. First, the resins that can yield diamond are only those pre-fired at temperatures between 500 and 1000 °C. Second, nevertheless, no diamond can be formed at 2 GPa from any of these resins. Third, temperatures in excess of 1500 °C are needed for diamond formation.

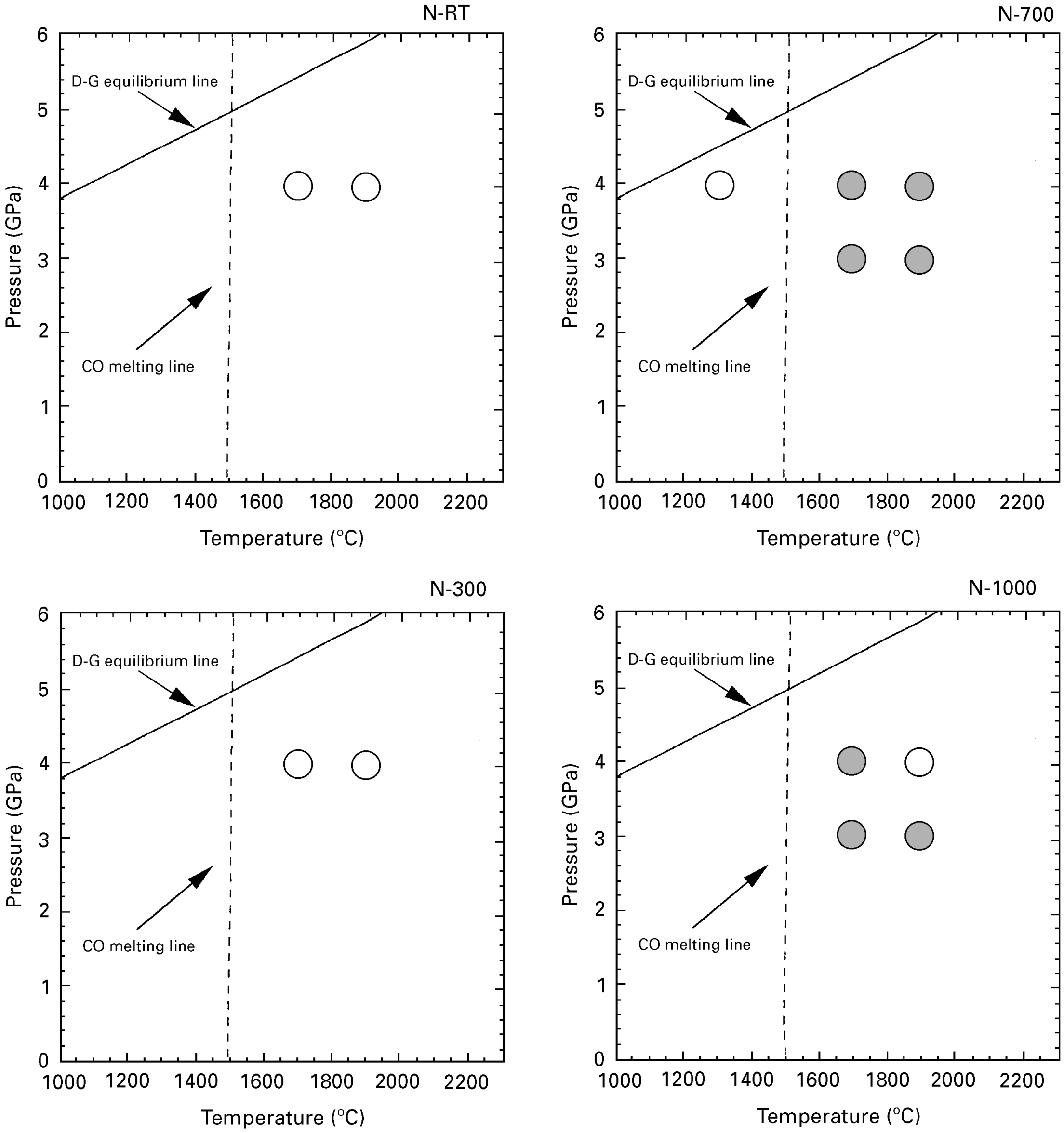
Figs 7 and 8 also indicate that the pressure–temperature conditions feasible for diamond synthesis depend on the pre-firing temperature. Roughly, the feasible areas widen with increase in the pre-firing temperature and then become narrower at higher pre-firing temperature. It turns out that the resins eventually have a common pressure–temperature point that is suitable for diamond formation. The location of the point is at 4 GPa and 1700 °C. At this specific pressure–temperature point, the amount of diamond synthesized is strongly governed by the pre-firing temperature. This is demonstrated in Fig. 9 for both the novolak and the resols. The amount of diamond, represented by the X-ray diffraction intensity of the diamond (111) reflection relative to the graphite (002) reflection, exhibits a maximum at 700 °C for the novolak and at 850 °C for the resols.

Also at the specific pressure–temperature point (4 GPa and 1700 °C), we carried out a reference experiment on the novolak pre-fired at 700 °C (N-700) without using cobalt. No diamond was formed, showing that the presence of cobalt or other solvent–catalyst is obviously required for diamond synthesis.

It should be noted that, in the present study, each high-pressure high-temperature treatment was accompanied by graphitization of the resins. The extent of graphitization varied according to the treatment pressure and temperature. We shall return to this point later in the discussion.

---

*Because there is no available data for the effect of pressure on the melting point of Co, we have assumed that there is essentially little pressure dependence of the melting temperature of Co. This is similar to the cases of other transition metals such as Fe and Ni.



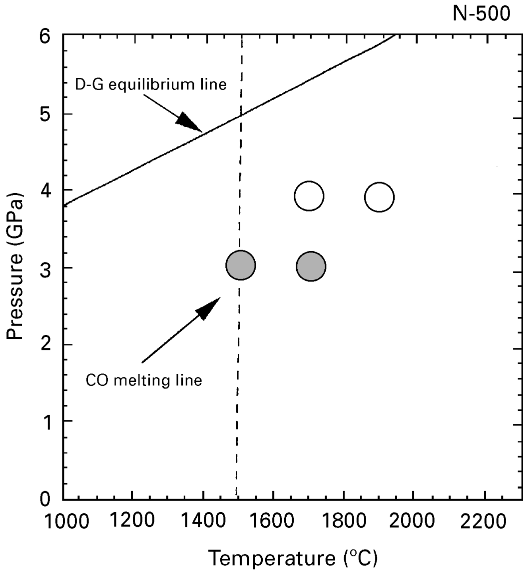


Figure 7 Pressure–temperature conditions and the major phases obtained from the novolak after 20 min. (●), diamond; (○), graphite. At the top right of each diagram, N denotes the novolak and the numbers represent the pre-fired temperature. N-RT is the unfired sample. The solid line represents a calculation for the diamond–graphite equilibrium [16] and the broken line is the melting temperature of cobalt against pressure [17].

3.3. Characterization of the synthesized diamond

Approximately ten pieces of diamond crystals of widths 0.3–0.7 mm were yielded from an experiment at 4 GPa and 1500 °C on the resols pre-fired at 850 °C (R-850). The crystals were pale yellow in colour. As shown in Fig. 10, most of the crystals had a cubo-octahedral habit with the $\{111\}$ and $\{100\}$ faces. Occasionally, $\{113\}$ faces were grown.

An interferometric micrograph on a (100) face is shown in Fig. 11, demonstrating the distribution of dendrites over the face. These were observed also on the $\{111\}$ and $\{113\}$ faces. The dendritic patterns appear distinctively in synthetic diamond and are believed to be an imprint of molten metal catalysts [18–22].

Fig. 12 shows Raman scattering spectra taken for one of the cubo-octahedral crystals. The measurements were made in two directions: parallel and perpendicular to the incident beam. We also show in Fig. 12 a spectrum of natural type Ib crystal which is employed for an anvil to generate a high pressure in diamond-anvil cells. The spectra of our diamond and the natural diamond are very similar to each other. A strong peak is located at

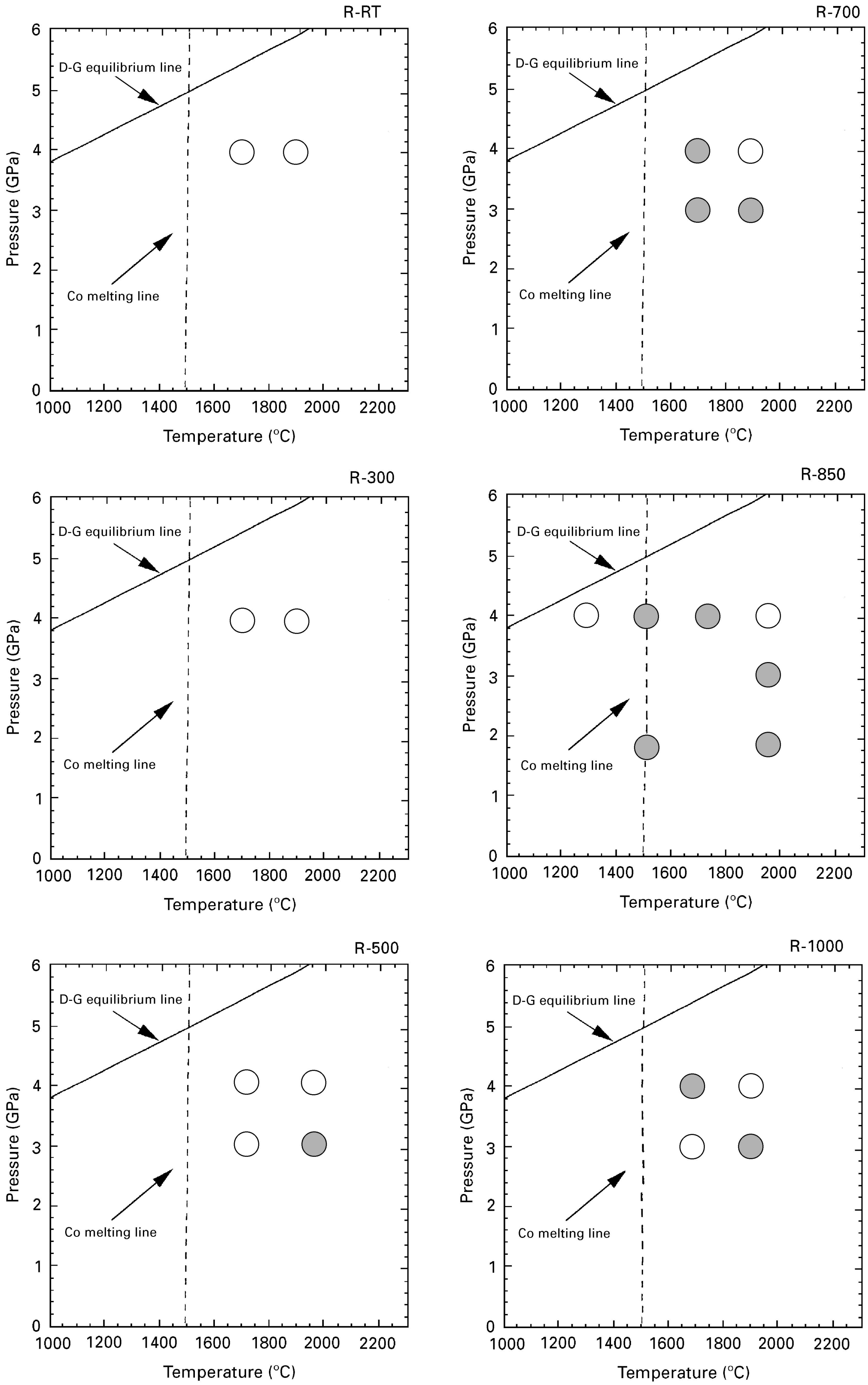


Figure 8 Pressure–temperature conditions and the major phases obtained from the resols after 20 min. (●), diamond; (○), graphite. The letters at the top right of each diagram represent the same as in Fig. 2. The lines have the same meanings as in Fig. 7.

1332 cm^{-1}, arising from the zone-centre optical phonon modes [23].

An absorption spectrum in the visible region is shown in Fig. 13. The location of absorption edge near 550 nm suggests that the diamond synthesized is type Ib in which nitrogen is present in dispersed form [24]. Generally, type Ia diamonds including aggregated nitrogen exhibit absorption edge at a much shorter wavelength [25].

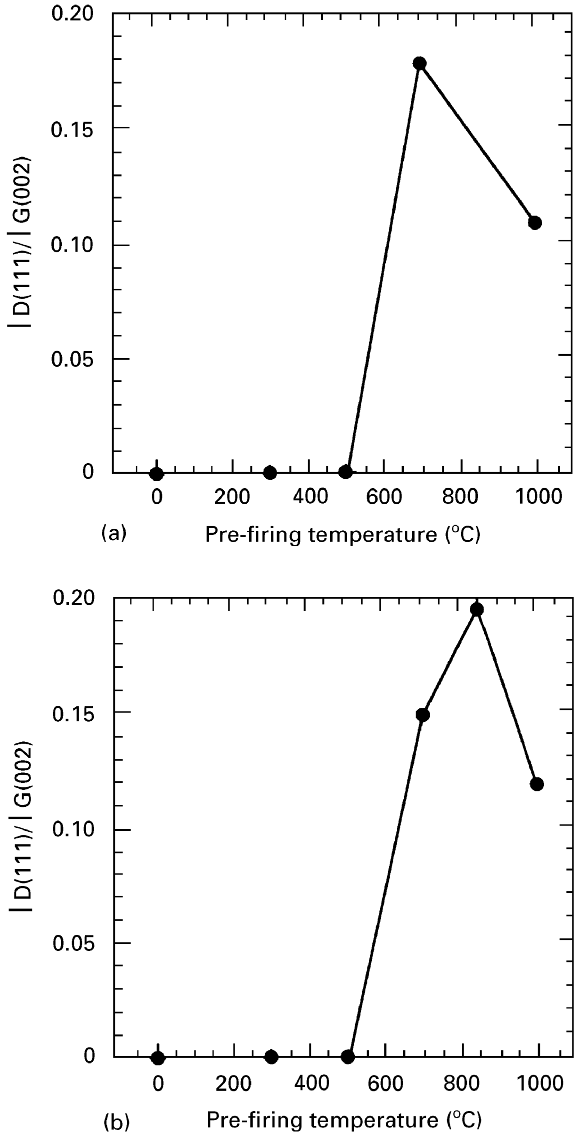


Figure 9 Relative amount of diamond as a function of pre-firing temperature for (a) the novolak and (b) the resols. The amounts were derived from the ratio of the intensities of diamond (111) reflection and graphite (002) reflection on the X-ray diffraction patterns of the retrieved samples after being treated at 4 GPa and 1700 °C.

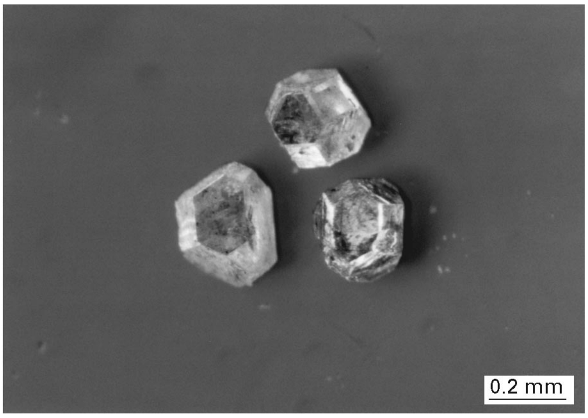


Figure 10 Diamond crystals synthesized at 4 GPa and 1500 °C from R-850. The crystals exhibit cubo-octahedral habits.

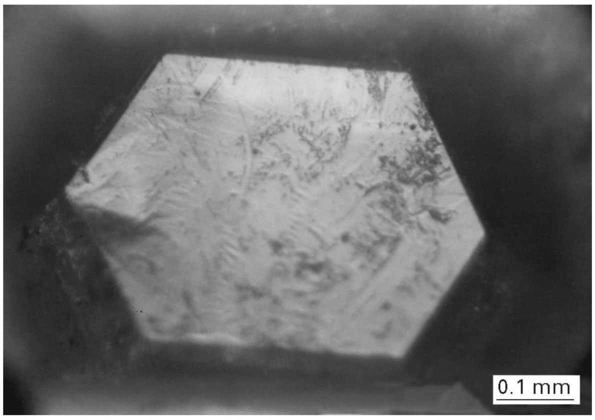


Figure 11 Interferometric image of a {100} face of a diamond crystal synthesized at 4 GPa and 1500 °C from R-850.

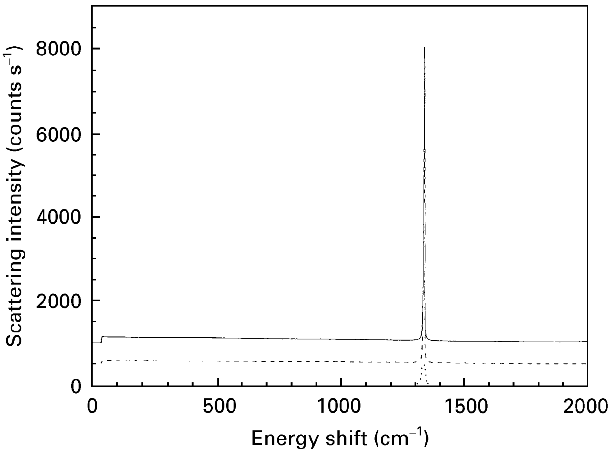


Figure 12 Raman scattering spectra of a diamond crystal synthesized at 4 GPa (—, – – –) and 1500 °C from R-850 and a natural diamond crystal (. . . . .). The spectra were recorded with 90° geometry with a triple monochromator (Japan Optics TSR-600) with a charge-coupled device detector (Photometsocs 512) using an incident beam from an Ar-ion laser. The measurements were made in directions parallel (—, ...) and perpendicular (– – –, ...) to the incident beam.

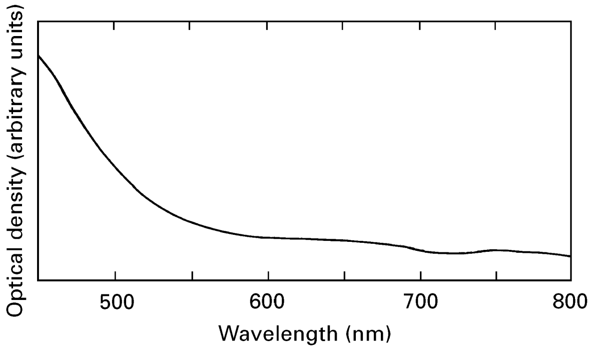


Figure 13 Visible absorption spectrum of a diamond crystal synthesized at 4 GPa and 1500 °C from R-850. The spectrum was recorded with a grating monochromator (Narumi 1 m) with a photomultiplier (Hamamatsu Photonics R943-02) using an incident beam from a tungsten lamp.

Fig. 14 shows an infrared absorption spectrum. Among the absorptions, two bands featured at 1126 and 1342 cm^{-1}, labelled by arrows, are in particular characteristic of type Ib diamond. The two bands have been ascribed to single-phonon absorption (normally at 1130 cm^{-1}) and local-mode absorption (at 1344 cm^{-1}), respectively [26]. In addition, the profile of the spectrum in Fig. 14 is

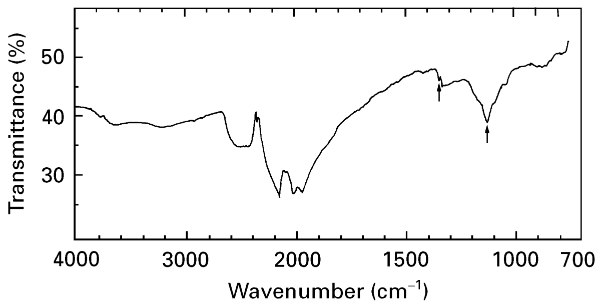


Figure 14 Infrared absorption spectrum of a diamond crystal synthesized at 4 GPa and 1500 °C from R-850. The spectrum was recorded with a micro-infrared spectrometer (Shimadzu AIM-8000 + FTIR-8200). See text for the bands labelled by arrows.

basically similar to those of synthetic type Ib diamonds [25].

4. Discussion

4.1. Thermodynamics

The following discussion is based on our X-ray diffraction analysis on the samples after the high-pressure high-temperature treatment. Fig. 15 shows X-ray diffraction patterns of R-850 heated at various temperatures under a pressure of 4 GPa. A sudden change in the patterns takes place between 1500 and 1700 °C. The change reflects a conspicuous approach of the turbostratic structure towards graphite. It is highly plausible that the chemical potential of the sample changes in a similar manner. Fig. 16 shows a schematic drawing of curves of the chemical potential, μ, versus temperature, T, for diamond, for graphite and for the phenolic resin at three different pressures. The phenolic resin curves are drawn according to the above presumption and also to our observation on a furan resin in which the graphitization temperature is lowered with increasing pressure [7, 9]. At temperatures where the chemical potentials of the diamond and graphite curves meet, diamond is in equilibrium with graphite. A trajectory of such temperatures, T_1, T_2 and T_3, against pressures, P_1, P_2 and P_3, yield the graphite–diamond equilibrium line. Crossing of the phenolic resin curve with the diamond curve takes place definitely at higher temperatures ($T_1 + \Delta T_1$ and so on). As shown in Fig. 17, the resultant trajectory P–D of the phenolic resin–diamond equilibrium points is located higher in temperature (i.e., lower in pressure) relative to the graphite–diamond equilibrium line G–D. Arising from the sudden approach of the chemical potential of the phenolic resin towards graphite, the phenolic resin–diamond equilibrium line exhibits an s-like curve. Among the reaction diagrams shown in Figs 7 and 8, those of N-1000, R-700 and R-850 roughly meet the pressure–temperature conditions bounded by such curves.

4.2. Mechanism of the diamond formation

The reference study has unambiguously indicated that cobalt is required as the catalyst for the diamond formation. It does not, however, necessarily mean that the presence of cobalt is sufficient. In the experiments when cobalt was present, diamond was synthesized only at temperatures on and above the melting point of cobalt (Figs 7 and 8), thus requiring the cobalt to be molten. This is also supported by the microtopograph showing the imprint of molten texture (Fig. 11). These observations imply that cobalt served as a catalyst–solvent, similar to the case of conventional diamond synthesis from graphite in the diamond-stable region on the carbon phase diagram [17, 27]. The phenolic resins are believed to be dissolved into the cobalt melt and thereupon, with the aid of cobalt, to construct sp^3 (tetrahedral) bonds that are readily changeable to diamond. Such solubility along with the capability to form sp^3 bonds are attached to the resins pre-fired at specific temperatures (500–1000 °C). The catalyst should not be simply limited to cobalt. Other transition metals such as iron and nickel could be other possibilities.

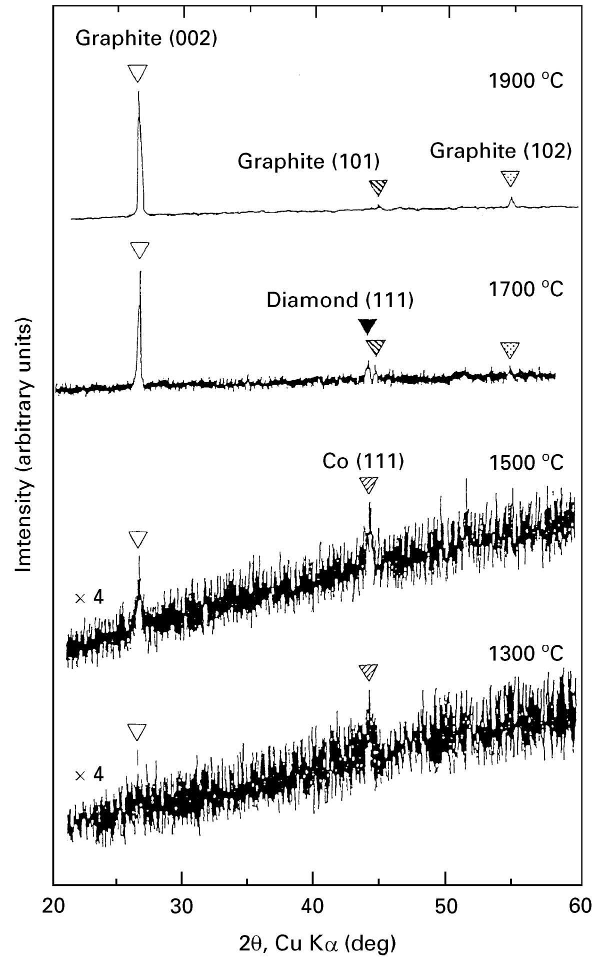


Figure 15 X-ray diffraction patterns of R-850 after being treated at various temperatures under a pressure of 4 GPa.

Brannon and McCollum [5] suggested that atomic hydrogen present in the pre-fired phenolic resin (novolak in their case) helped the growth of diamond. The hydrogen content was 4.85 wt% in their sample pre-fired at 500 °C. This quantity is eventually at a level very near to our sample pre-fired at the same temperature (Table II). We have shown that the pertinent temperature (500 °C) is the lower bound for pre-firing the resins suitable for diamond synthesis. Much higher temperatures (700 °C or higher) are needed in

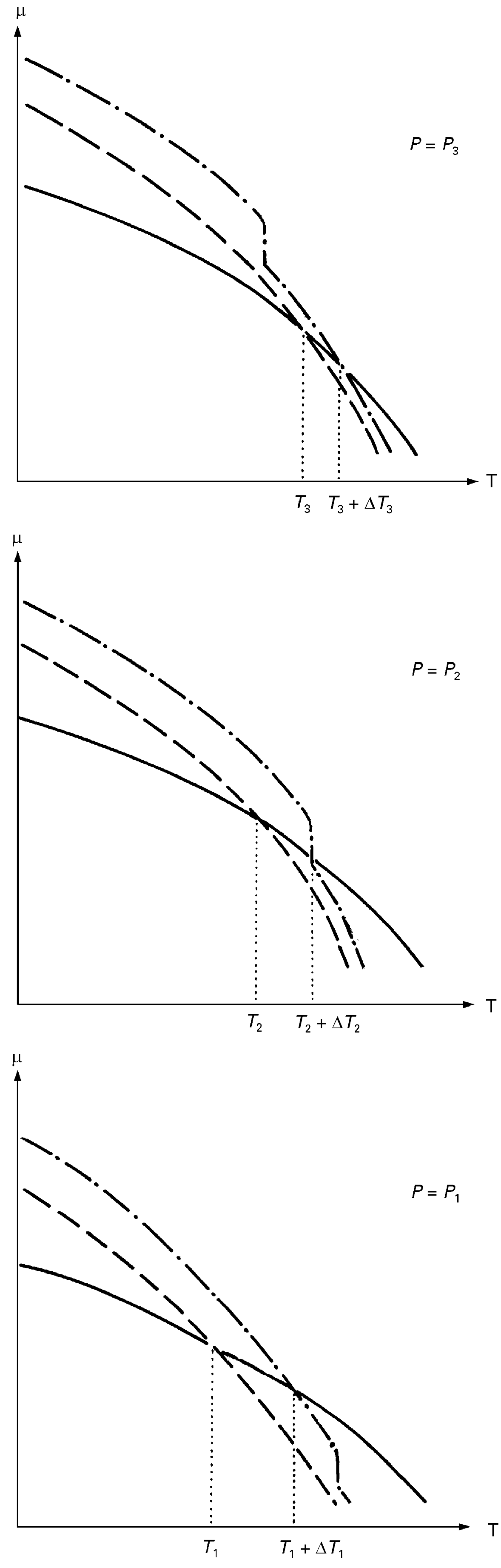


Figure 16 Schematic drawing of the chemical potential, μ, versus temperature, T, for diamond (——), graphite (———) and phenolic resin (—·—) at pressures P_1, P_2 and P_3. The pressures are in the order $P_1 < P_2 < P_3$. In each diagram, the chemical potential of phenolic resin suddenly approaches that of graphite at each specific temperature.

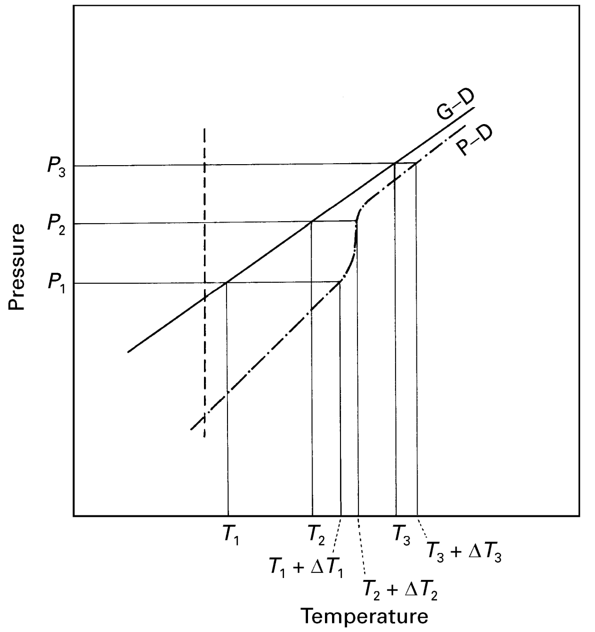


Figure 17 Graphite–diamond equilibrium line G–D (——) and phenolic resin–diamond equilibrium line P–D (—·—). The line representing the melting point of the cobalt catalyst–solvent (– – –) is also shown.

order that the diamond formation proceeds much more easily. At such temperatures, the hydrogen content is significantly decreased, as demonstrated in Table II. It is rational from these considerations to assume that atomic hydrogen played little role in the formation of diamond.

Instead, the radicals in the resins strongly govern the diamond formation in the present work. Niedbalska and co-workers [2–4] noted earlier the importance of free radicals and mentioned that the radical concentration of their sample reached a maximum at 650 °C [3]. This temperature is eventually quite close to the mean of the temperatures at which our two resins, respectively, exhibit a maximum in the amount of radical concentration. In our case, as shown in Table I, the radical concentration reaches a maximum at 500 °C in the novolak and at 700 °C in the resols. We have shown in Fig. 9, on the other hand, that the temperatures at which the diamond formation exhibits a maximum are 700 and 850 °C for the novolak and resols, respectively, demonstrating significant correspondences within 200 and 150 °C between the radical concentration and the relative amount of diamond formed. Also, the temperatures at which the radicals begin to develop (Table I) are the same as the lower bounds in pre-firing temperatures that are adequate for the diamond formation (Fig. 9). These facts imply that the resins suitable for the diamond formation should be quite chemically active prior to the high-pressure treatment. This activity helped the prefired resins readily to dissolve into the cobalt melt and to construct the tetrahedral bonds which, in turn, aggregate into a diamond network.

5. Conclusions

The present study has revealed that the synthesis of diamond is feasible from phenolic resins under the conditions where graphite is thermodynamically stable on the carbon phase diagram and, hence, supports the earlier relevant experiments [2–5]. The salient features derived anew in this study are as follows.

1. There is no preference in the choice of the resin, whether novolak or resols.
2. The resins suitable for the diamond formation are those that are pre-fired at temperatures between 500 and 1000 °C so as to become carbon precursors almost having lost hydrogen and oxygen, obtaining free radicals and being turbostratic.
3. Cobalt serves as a catalyst–solvent, as inferred from the temperature conditions required for the diamond synthesis and from the microtopograph of diamond faces.
4. The pressure–temperature conditions for the diamond synthesis are within a region bounded by an s-shaped line that can be qualitatively delineated from a thermodynamic argument.
5. The diamond crystals are type Ib as evidenced by the infrared and visible absorption measurements.

Acknowledgements

We are grateful to the people at Sumitomo Dures Co. for supplying us with the phenolic resins. Thanks are also extended to Professor M. Kobayashi and Dr Y. Mita for the visible absorption experiment and to Professor S. Sugai for the Raman scattering measurement.

References

1. H. O. PIERSON, "Handbook of carbon, graphite, diamond and fullerenes" (Noyes Publications, Park Ridge, NJ, 1993).
2. A. NIEDBALSKA and A. SZYMAŃSKI, in "Proceedings of the 25th Annual Meeting of the European High Pressure Research Group", Potsdam, August 1987 (Akad. Wissenschaften DDR. Potsdam, 1987) p. 34.
3. A. NIEDBALSKA, *High Press. Res.* **5** (1990) 708.
4. A. NIEDBALSKA, A. SZYMAŃSKI and S. A. ZALEWKI, in "Science and technology of new diamond", edited by S. Saito, O. Fukunaga and M. Yoshikawa (KTK Scientific Publishers, Tokyo, 1990) p. 229.
5. C. J. BRANNON and S. L. MCCOLLUM, in "New diamond science and technology", edited by R. Messier, J. T. Glass, J. E. Butler and R. Roy (Materials Research Society, Pittsburgh, PA, 1991) p. 117.
6. K. HIGASHI and A. ONODERA, *Physica B* **139–40** (1986) 813.
7. A. ONODERA, K.HIGASHI and Y. IRIE, *J. Mater. Sci.* **23** (1988) 422.
8. *Idem*, in "Science and technology of new diamond", edited by S. Saito, O. Fukunaga and M. Yoshikawa (KTK Scientific Publishers, Tokyo, 1990) p. 235.
9. O. ONODERA, Y. IRIE, K. HIGASHI, J. UMEMURA and T. TAKENAKA, *J. Appl. Phys.* **69** (1991) 2611.
10. A. ONODERA, K. SUITO and Y. MORIGAMI, *Proc. Jpn. Acad. B* **68** (1992) 167.
11. A. ONODERA, *High Temp. High Press.* **19** (1987) 579.
12. A. OHTANI, S. MIZUKAMI, M. KATAYAMA, A. ONODERA and N. KAWAI, *Jpn. J. Appl. Phys.* **16** (1977) 1843.
13. K. OUCHI, *Carbon* **4** (1966) 59.
14. S. MROZOWSKI, *ibid.* **9** (1971) 97.
15. *Idem*, *J. Low Temp. Phys.* **35** (1979) 231.
16. R. BERMAN and F. SIMON, *Z. Elektrochem.* **59** (1955) 333.
17. F. P. BUNDY, H. P. BOVENKERK, H. M. STRONG and R. H. WENTORF JR, *J. Chem. Phys.* **35** (1961) 383.
18. S. TOLANSKY and I. SUNAGAWA, *Nature* **184** (1959) 1526.
19. H. P. BOVENKERK, *Am. Mineral.* **46** (1961) 952.
20. S. TOLANSKY, *Proc. R. Soc.* **A 263** (1961) 31.
21. *Idem.*, *ibid.* **270** (1962) 443.
22. H. KANDA, M. AKAISHI, N. SETAKA, S. YAMAOKA and O. FUKUNAGA, *J. Mater. Sci.* **15** (1980) 2743.
23. S. A. SOLIN and A. K. RAMDAS, *Phys. Rev. B* **1** (1970) 1687.
24. H. B. DYER, F. A. RAAL, L. DU PREEZ and H. H. N. LOUBSER, *Phil. Mag.* **11** (1965) 763.
25. R. M. CHRENKO and H. M. STRONG, " Physical properties of diamond", General Electric Technical Information Series 75CRD089 (General Electric Co., Schenectady NY., 1975).
26. A. T. COLLINS and G. S. WOODS, *Phil. Mag. B* **46** (1982) 77.
27. H. P. BOVENKERK, F. P. BUNDY, H. T. HALL, H. M. STRONG and R. H. WENTORF JR, *Nature* **184** (1959) 1094.

Received 19th April
and accepted 19th December 1996