

Crystallization of amorphous carbon at high static pressure and high temperature

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Amorphous carbons prepared from furfuryl alcohol resin have been studied in a high-pressure apparatus of octahedral anvil type at pressures up to 18 GPa and at temperatures up to 2000° C. The amorphous carbons, when heated under pressure, crystallized first into graphite at 450 to 600° C and then into diamond at 1120 to 2000° C. The temperatures for the onset of these crystallizations, T_g and T_d , were determined by a simple technique. As the temperature for the preparation of the amorphous carbons was raised from 700 to 1000° C, T_g at 15 GPa increased slightly whereas T_d at the same pressure turned from a decrease into an increase beyond 750° C for the preparation temperature. For amorphous carbon prepared at 850° C, T_g increased a little while T_d decreased markedly with increasing pressure.

1. Introduction

Diamond is one of the most intriguing materials. It is the hardest material known on earth. Diamond has a thermal conductivity higher than that of copper at room temperature. These facts permit using diamond for industrial applications; abrasives, cutting tools, solid-state electronic devices, etc. Diamond for industrial use is now to a great part synthetic. Methods (see e.g. [1]) of synthesizing diamond can roughly be classified into four categories; (i) catalytic synthesis under high static pressure around 5 GPa, (ii) non-catalytic synthesis at high static pressure exceeding 11 GPa, (iii) non-catalytic synthesis with dynamic compression, and (iv) decomposition of organic compounds at reduced pressure.

The non-catalytic process in combination with high static pressure has been relatively unexplored, primarily because the pressure needed for the process has been far beyond the scope of industrial installations. The process was first reported by Bundy [2], who studied various carbons at pressures higher than 11 GPa[†]. By the use of a flash-heating technique for attaining transient high temperatures over 3000 K, graphite was directly converted into diamond. A similar study was carried out by Wakatsuki *et al.* [3]. In contrast to the above two studies by dynamic heating, a technique to statically heat up the sample was employed later. Vereshchagin *et al.* [4] heated graphite up to about 3000° C by directly passing an electric current through the sample and converted graphite into diamond. This static heating was also done by Naka *et al.* [5] at 14 GPa and by Onodera *et al.* [6] beyond 14 GPa.

Since the non-catalytic diamond formation is basically a non-equilibrium process, it is governed by

non-chemical free energy which in turn is affected by the nature of the start material, stress anisotropy, and so forth. In fact, Wentorf [7] reported that highly refined natural graphite was most easily transformed into diamond among the elemental carbons he exposed to pressures of 10 to 12 GPa and temperatures of 1300 to 3000° C. Bundy and Kasper [8] clarified that hexagonal diamond can be formed only from single-crystal or well-crystallized polycrystalline graphite.

For boron nitride (BN), which is an analogue of carbon, Wakatsuki and co-workers [9, 10] demonstrated that a start sample of graphite-type BN with low crystallinity was readily converted into the zincblende form (analogous to diamond). Frantsevich *et al.* [11] reported a similar effect. Both groups also showed [11, 12] that well-crystallized graphite-type BN can form wurtzite-type BN, in accord with the formation of hexagonal diamond [8].

We have shown earlier [13] that amorphous BN can be converted into the zincblende form under pressure-temperature conditions comparable to those used with low-crystallinity graphite-type BN [9-11]. Along this line, we have studied amorphous carbon and have given a brief report [14] about the synthesis of diamond from amorphous carbon under static pressure. In the course of that study it became clear from monitoring of the electrical resistance of the sample while under pressure that graphitization of amorphous carbon proceeded prior to the formation of diamond. We have studied these crystallizations in more detail by changing the grade of amorphous carbon. This paper describes the crystallization behaviour of amorphous carbon at high static pressures up to 18 GPa and at temperatures up to 2000° C.

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† The pressures mentioned in publications appearing earlier than 1970 are all changed herein into a new pressure scale due to the downward revision.

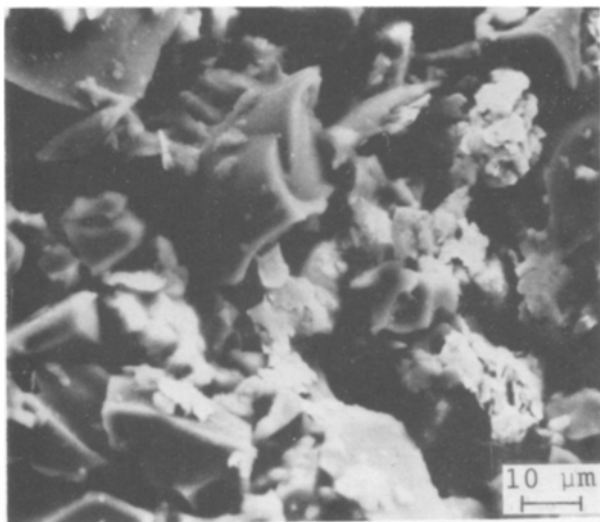


Figure 1 SEM photograph for aC-750.

2. Experimental procedure

2.1. Preparation of start material

The amorphous carbon for high-pressure, high-temperature studies was obtained as follows. First, furfuryl alcohol resin was prepared by addition of *p*-toluenesulphonic acid (70 wt% in water) onto furfuryl alcohol. Then, the resin was fired under N₂ gas at various temperatures between 700 and 1000°C. Amorphous carbons with various grades were obtained according to the firing temperatures. Henceforth the firing temperature is given as a number with each amorphous carbon; for example aC-750 represents the amorphous carbon prepared at 750°C.

Fig. 1 shows a scanning electron microscope (SEM) photograph for aC-750, exhibiting a blocky shape. A transmission electron microscope (TEM) photograph and an electron diffraction pattern of aC-850 are shown in Figs 2a and b, respectively. Table I gives typical impurity levels for aC-750 and aC-850, together with other materials.

Fig. 3 shows powder X-ray diffraction patterns for the amorphous carbons. Also, X-ray patterns of glassy carbon (GC; obtained from Tokai Carbons, Grade GC 20) and of spectroscopic graphite (SG; obtained from Shimadzu Industry, Grad S-8) are shown for comparison. As the preparation tem-

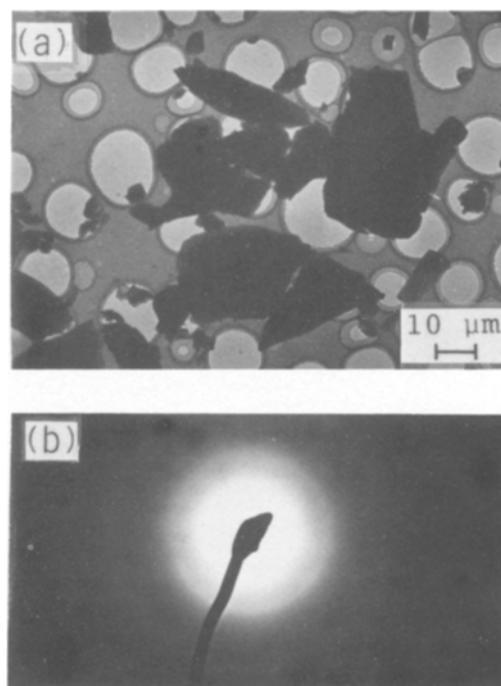


Figure 2 (a) TEM photograph and (b) electron diffraction pattern for aC-850.

perature is raised, the structure of the amorphous carbons approaches that of graphite.

In addition, the electrical resistivity of the amorphous carbons exhibits sequential changes relative to the preparation temperature. Fig. 4 shows the room-temperature resistivity of amorphous carbons measured at 15 GPa. As the preparation temperature is raised the resistivity of the amorphous carbons decreases toward that of SG.

However, no such sequential change was observed in the spectra of Raman shift or infrared (IR) absorption, measured on pellets mixed pressed with KBr powder.

2.2. High-pressure experiments

For high-pressure experiments an apparatus of octahedral anvil type [15] was employed. The sample to be studied was embedded in an octahedral sample cell as shown in Fig. 5. Either molybdenum or silver disks were used for the electrodes which were in contact

TABLE I Typical impurity levels for the samples and pressure media

Sample	Composition (%)			Composition (p.p.m.)						
	H	O	N	Ti	Cr	Mn	Fe	Ni	Al	Si
aC-750 [‡]	1.8	3.0	0.24	2	9	0	20	0	20	20
aC-850 [‡]	1.1	2.3	0.36	2	65	7	90	0	200	100
GC [§]	*	*	*	100	100	65	400	65	1%	900
SG [¶]	*	*	*	0	0	0	7	0	4	90
pyrophyllite ^a	*	*	*	0.3%	9	0	900	100	†	†
BN ^b	*	*	*	0	20	9	200	0	900	900

*Not measured.

†Al and Si contained according to the composition.

‡Metals not detected: Zr, V, Mo, W, Co, Sb, Ru, Rh, Pd, Ir, Pt, Ta, Hf, Nb.

§Metals detected other than the list: Na 100 p.p.m., K 90 p.p.m., Mg 400 p.p.m., Ca 100 p.p.m., B 0.2%.

¶Metals detected other than the list: Na 4 p.p.m., K 2 p.p.m., Mg 2 p.p.m., B 65 p.p.m.

^aChemical composition: Al₂Si₄O₁₀(OH)₂. Metals detected other than the list: Na 400 p.p.m., K 900 p.p.m., Mg 7 p.p.m., Ca 4 p.p.m., V 900 p.p.m., Mo 20 p.p.m., B 100 p.p.m., Ir 100 p.p.m., Ta 20 p.p.m.

^bGraphite-type (g-BN). Metals detected other than the list: Na 100 p.p.m., K 200 p.p.m., Mg 200 p.p.m., Ca 1%.

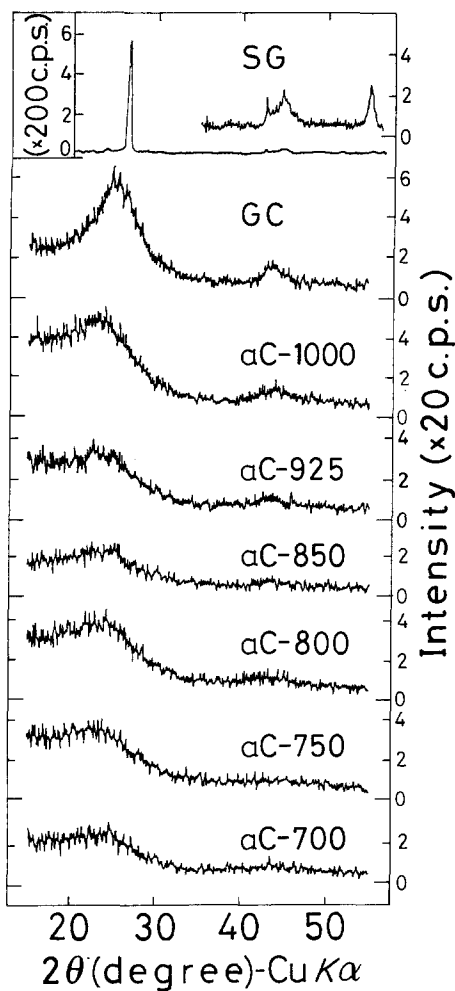


Figure 3 X-ray diffraction patterns for the samples to be studied at high pressure and high temperature.

with the sample. The two metals are not known as catalysts for diamond synthesis.

The sample was heated at various fixed pressures by passing an alternating current through it. The current and corresponding voltage applied to the sample were

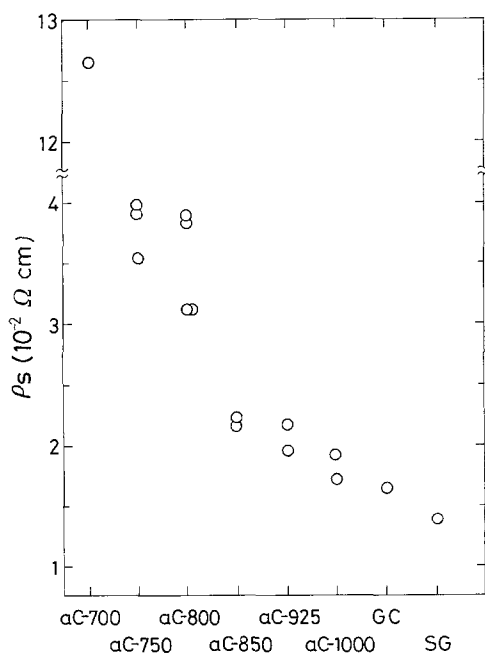


Figure 4 Electrical resistivity of the samples at 15 GPa and room temperature. The abscissa is not to scale.

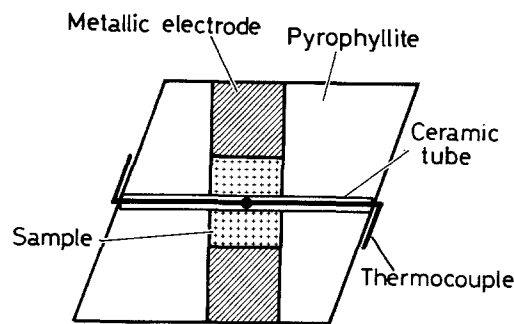


Figure 5 A cross-section of an octahedral sample cell.

monitored in each experiment. A Pt/Pt-13% Rh thermocouple was used for temperature measurement. The thermocouple wire was sheathed with a ceramic tube (Fig. 5) in order to prevent a possible catalytic function for diamond formation, because both platinum and rhodium are known as catalysts [16]. No correction was made for the effect of pressure on the e.m.f. of the thermocouple.

3. Results

3.1. 15 GPa experiments

Fig. 6 shows typical examples of current-voltage relation for the various amorphous carbons measured at a pressure of 15 GPa. Relations for GC and SG are also shown for comparison. The current-voltage relation gives basically the electrical resistance of the sample under study. A general feature perceived from Fig. 6 is that there appear two anomalies in the relation for the amorphous carbons; one an abrupt rise of the current (namely, a decrease of the resistance) and the other a decrease of the current (an increase of the resistance). An eventual rise of the current is also seen in GC, but is not observed in SG.

In order to elucidate the behaviour of the amorphous carbons along the current-voltage relations (Fig. 6), the samples heated at various temperatures were retrieved and X-rayed. Fig. 7 shows Debye-Sherrer X-ray diffraction photographs of the start sample and the samples retrieved from 15 GPa. Fig. 7a gives an X-ray diffraction photograph of aC-850 under ambient conditions showing a halo pattern. The sample retrieved from 15 GPa and 500°C remains in the amorphous state as shown in Fig. 7b. In Fig. 7c,

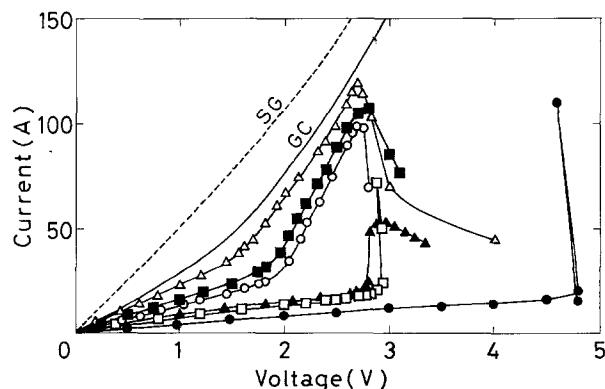


Figure 6 Current-voltage relations for the samples at 15 GPa. The duration at each point is mostly 30 sec. (●) aC-700, (□) aC-750, (▲) aC-800, (○) aC-850, (■) aC-925, (△) aC-1000.

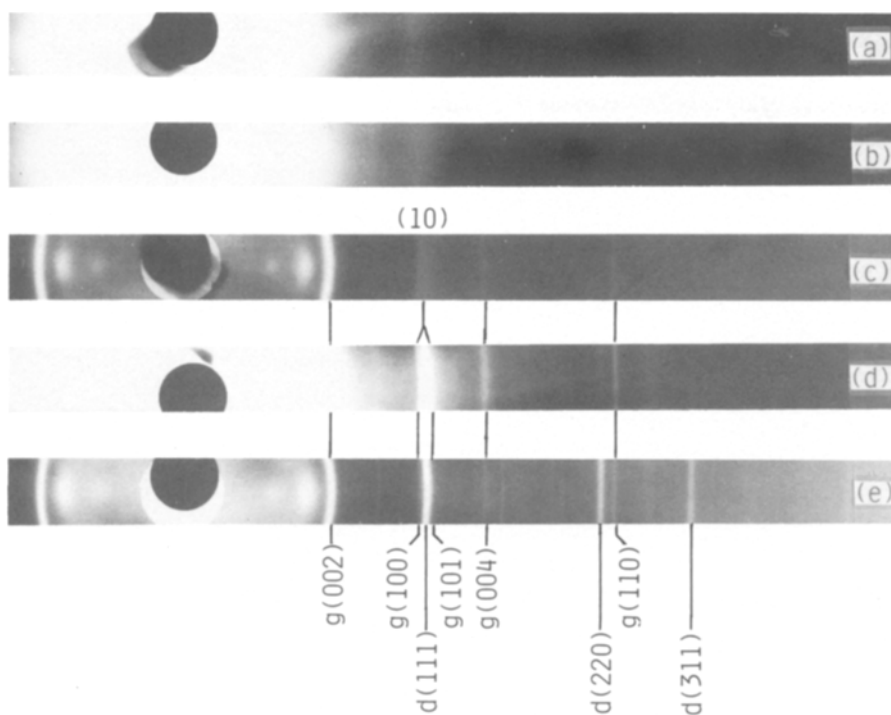


Figure 7 Debye-Scherrer X-ray diffraction photographs for aC-850: (a) ambient conditions; (b) retrieved from 15 GPa, 500°C; (c) retrieved from 15 GPa, 1000°C; (d) retrieved from 15 GPa, 1300°C; (e) retrieved from 15 GPa, 1350°C. In (e), the spotty reflections are from the ceramic tube (Fig. 5) next to the sample and mixed retrieved with it. g and d for the reflection indices represent respectively graphite and diamond.

a strong (002) reflection from graphite appears indicating that the sample has crystallized into graphite below 1000°C. This temperature is realized between the rise and drop of the current in Fig. 6. In Fig. 7d the (10) band has been split into graphite (100) and (101) reflections below 1300°C. After the eventual drop in the current at 1350°C, diamond is formed as seen from Fig. 7e.

It is apparent from the above demonstration that the eventual rise and drop of the current passing through the sample (Fig. 6) are respectively associated with the onsets of graphitization and diamond formation. The eventual rise of the current for GC is then ascribed to crystallization of GC into graphite. Also, the absence of an abrupt rise of current for SG is well

explained because the sample is already in the graphite phase. Consequently, the onset temperatures for graphitization (T_g) and diamond formation (T_d) can be obtained from such current-voltage relations as exemplified in Fig. 6.

Fig. 8 gives plots of T_g and T_d obtained at 15 GPa for the amorphous carbons, GC, and SG. The data points are obtained from Fig. 6 and other separate experiments. A general trend in Fig. 8 is that T_g increases slightly as the preparation temperature is raised. On the other hand, T_d differs remarkably among the amorphous carbons; T_d increases as the preparation temperature is raised. However, the lowest T_d , 1120°C, is observed for aC-800. Also, it should be noted that T_d for aC-700 (not shown in Fig. 8) is greater than 2000°C.

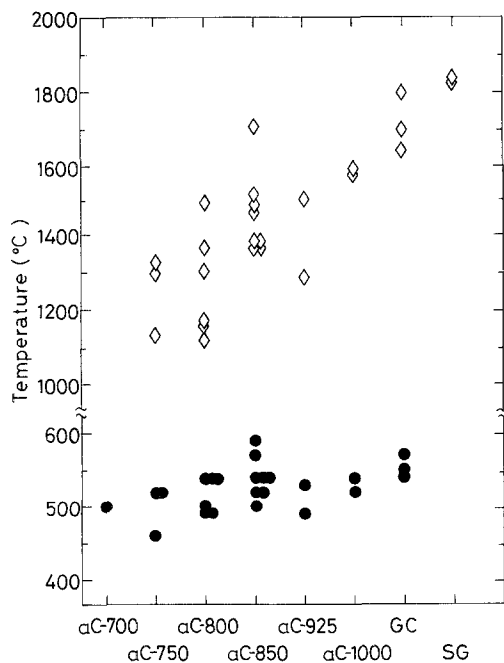


Figure 8 Onset temperatures for (●) graphitization and (◇) diamond formation for various samples. The abscissa is not to scale.

3.2. aC-850 experiments

Fig. 9 shows current-voltage relations for aC-850 measured at various pressures. At 8 GPa, the sample undergoes graphitization at a temperature of 470°C, as seen from the eventual increase of the current. However, there appears no drop in the current on further heating, suggesting that diamond is not formed. At pressures higher than 10 GPa, formation of diamond takes place as evidenced by the drops in the current (Fig. 9).

The temperatures for the onsets of graphitization and diamond formation for aC-850, obtained from Fig. 9 and other experiments, are plotted in Fig. 10 as a function of pressure. Essentially, T_g increases with pressure from about 470°C at 8 GPa up to 590°C at 18 GPa. Since T_g at ambient pressure is higher than 2000°C, the application of pressure to 8 GPa causes a remarkable decrease of T_g .

In Fig. 10, T_d decreases markedly with increasing pressure from 10 to 18 GPa. This trend is similar to those observed by Bundy [2] using dynamic heating technique and by us [6] with a static heating technique,

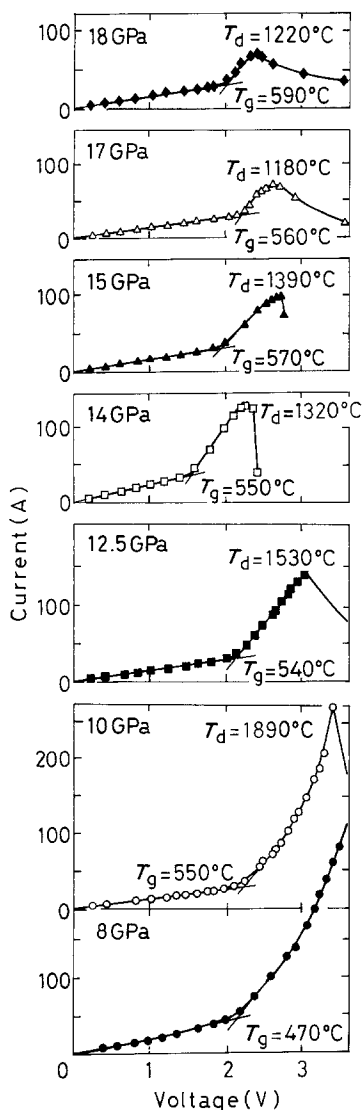


Figure 9 Current–voltage relations for aC-850 at various pressures. The duration at each point is mostly 30 sec.

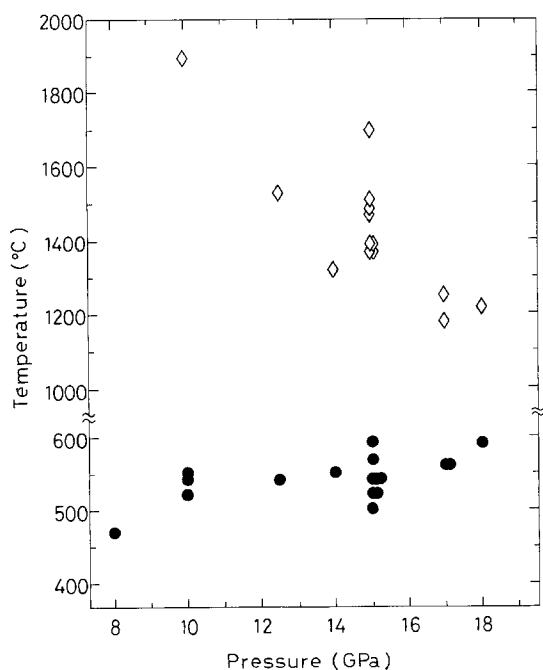


Figure 10 Onset temperatures for (●) graphitization and (◇) diamond formation as a function of pressure for aC-850.

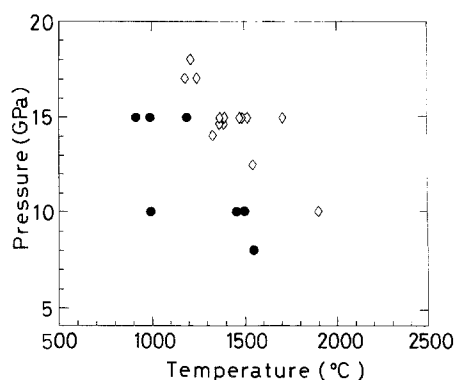


Figure 11 Pressure–temperature plots of phases present in the retrieved samples. (●) Graphite formed, (◇) diamond formed.

both studied for the direct conversion of graphite into diamond. The T_d values in Fig. 10 are, however, significantly lower than the temperatures [2, 4, 6] for the direct graphite-to-diamond conversion.

3.3. Retrieval experiments

In addition to the measurements of the onset temperatures of graphitization and diamond formation, some more experiments were undertaken to retrieve the sample after the high-pressure, high-temperature treatments. The retrieved samples were subjected to X-ray diffraction, electron diffraction and TEM.

Fig. 11 shows pressure–temperature plots of the phases present in the retrieved samples for aC-850. Each point in Fig. 11 is essentially higher in temperature than the onset temperatures in Fig. 10, because the retrieval was done after the completion of graphitization or diamond formation was confirmed from current–voltage relation.

Fig. 12a shows an electron diffraction pattern of aC-850 which was retrieved from 15 GPa. The pattern can be unequivocally assigned to diamond. Fig. 12b shows a TEM photograph of the sample giving the pattern in Fig. 12a. The diamond particles are very small, with sizes less than $0.1 \mu\text{m}$.

4. Discussion

We have demonstrated here that the amorphous carbons of various grades undergo crystallization at high static pressures and high temperatures. The crystallization is twofold: graphitization and diamond formation. At 15 GPa, T_g increases slightly with an increase of the temperature for preparing each amorphous carbon. For a given amorphous carbon, aC-850, T_g decreases from an ambient value of beyond 2000°C down to approximately 470°C at 8 GPa and then increases up to 590°C as the pressure is elevated to 18 GPa (Fig. 10). On the other hand, the change of T_d at 15 GPa turns from a decrease into an increase as the preparation temperature is raised beyond 750°C . A marked decrease of T_d with increasing pressure is observed for a given amorphous carbon, aC-850 in this case.

Some comments may be needed about the absence of an impurity effect on the diamond formation and about the reliability of the temperature measurements. First, electron probe microanalysis (EPMA)

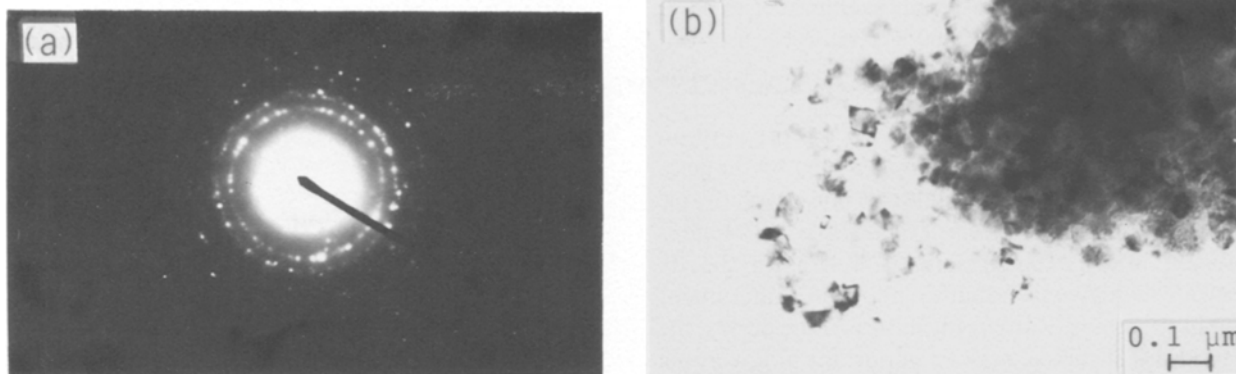


Figure 12 (a) Electron diffraction pattern and (b) TEM photograph of diamond formed from aC-850.

inspections of the diamond-bearing samples have shown no existence of known catalyst-solvent metals, iron and nickel for example, on or near the diamond. Second, replacing part of the pressure cell from pyrophyllite into BN (see Table I) has yielded quite a similar result in the formation of diamond. Third, the marked negative slope of T_d against pressure (Fig. 10) and the low T_d values observed below 1200°C (Figs 8 and 10) cannot be interpreted from an extrapolation of the temperatures needed for the catalytic diamond synthesis at lower pressures [16]. Fourth, there seems to exist no correlation between T_d and the amount of gaseous residue in the amorphous carbons shown in Table I. Fifth, the difference of T_d values among the amorphous carbons as well as between the amorphous carbons and SG cannot be explained by the catalyst-solvent mechanism because in that case the threshold temperature (which corresponds to T_d in our case) is governed by the melting point of a given eutectic [16]. Sixth, the temperature measurement is substantiated by a fair agreement of our melting experiment on silver at 15 GPa with a proposed melting curve for this material [17]. It is likely from the above discussion that the formation of diamond in this study presumably proceeds uncatalysed.

Previous work on pressurizing amorphous carbon or similar material have all reported the formation of diamond. Bundy [2] in his study of the conversion of graphite into diamond also flash-heated amorphous carbon at a static pressure of about 11.6 GPa. Hirano *et al.* [18] have shown that under static pressures of 9 and 10 GPa glassy carbon crystallized into graphite and diamond began to be formed after completion of the graphitization. The formation of diamond took place in this case beyond 2300°C at 9 GPa and above 1800°C at 10 GPa. This downward change of the temperature of diamond formation with pressure is in accordance with the present data. Under dynamic compression, amorphous carbon was directly converted into diamond [19]. Sometimes hexagonal diamond was formed, depending on the pressure and temperature [19, 20]. Samples similar to our amorphous carbon but prepared at lower temperatures were shocked to 100 GPa, again forming diamond [21].

The effect of amorphization of the start material has not been clarified in many of the previous reports cited above, whereas it is clear in the synthesis of the zinc-

blende form of BN [13]. On the other hand, Wentorf [7] demonstrated that highly refined natural graphite could most easily form diamond at temperatures as low as 1300°C under a static pressure of 12.5 GPa. In Wentorf's study carbon blacks also yielded diamond at that same pressure but at a higher temperature, 2000°C. The present study has shown from Fig. 8 that the amorphous carbons (apart from the well-crystallized form of carbon, namely SG) can more easily form diamond; for aC-700, however, diamond can only be formed above 2000°C. This trend is against that studied by Wentorf [7], but agrees with our study on BN [13].

Anyway, one of the most important points among the present results is the strong dependence of T_d upon the grade of the amorphous carbons, in contrast to the weak dependence of T_g on the grade. The weak dependence of T_g on the preparation temperature suggests that the graphite phases formed after crystallization from the different amorphous carbons are similar to each other. This similarity would presumably lead to similar values of T_d , being formed from similar graphites. On the contrary, our experiments have yielded a marked dependence of T_d on the preparation temperature. This suggests the existence of a species other than the graphite phase already crystallized. Likewise, the fact that T_d values in Fig. 9 are significantly lower than the temperatures for direct graphite-to-diamond conversion [2, 4, 6] also suggests an existence of such a species that is not graphitized but is instead readily converted into diamond.

A plausible explanation of this is that our amorphous carbons are composed of two species; graphitizable and non-graphitizable. This description is in accord with earlier pictures [22, 23]. The graphitizable species contains sp^2 bonds while the non-graphitizable species is made up of tetrahedral sp^3 bonds. The graphitizable species easily crystallizes into graphite but is instead reluctant to be converted into diamond, and *vice versa* for the non-graphitizable species. The amorphous carbons prepared at lower temperatures are supposed to contain a larger amount of non-graphitizable species with stronger sp^3 bonds. It is likely that the non-graphitizable species is directly converted into diamond, whereas the graphitizable species crystallizes first into graphite followed by the formation of diamond at temperatures higher than for diamond

formation from the non-graphitizable species. The high T_d for aC-700 ($>2000^\circ\text{C}$) may be ascribed to incomplete construction of the non-graphitizable species.

The sequential change of T_d with the preparation temperature cannot simply be interpreted by the relative amounts of the graphitizable and non-graphitizable species because, as noted earlier, no sequential trend is observed in the Raman shift as well as in the IR spectra which give information about the amounts of sp^2 and sp^3 bonds. Rather, the nature of the bonds, the strength for instance, may be important in governing T_d .

5. Summary

We have prepared various grades of amorphous carbons by changing the firing temperature for preparing them from furfuryl alcohol resin. The grade can be envisaged from the powder X-ray diffraction patterns and also from the room-temperature resistivity at 15 GPa as well, but is not clear from the Raman shift or IR spectrum.

The amorphous carbons were heated at high static pressures by passing an alternating current through them. Both graphitization and the formation of diamond were determined from *in situ* monitoring of current-voltage relations during heating as well as from post-inspections of retrieved samples.

The effect of changing the preparation temperature on T_g at 15 GPa is small and positive, whereas that on T_d at 15 GPa turns from negative to positive as the preparation temperature is raised above 750°C . For aC-850, T_g increases a little while T_d decreases conspicuously as the pressure is elevated. The lowest T_d observed is 1120°C at 15 GPa for aC-800. This is significantly lower than the temperatures needed for the catalytic synthesis of diamond.

The results were interpreted by existing structure models proposed for amorphous carbon as composed of graphitizable and non-graphitizable species. It is suggested from the experiments that the nature of the bonds in these two species presumably governs the crystallization behaviour.

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