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Diamond synthesis by weak shock loading

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A hexagonal polymorph of diamond has been synthesized by relatively weak shock loading (in a range of projectile velocity 0.655 to 1.88 km sec^{-1}) with a recovery technique. Four mixtures of copper with spectroscopic graphite, amorphous carbon, glassy carbon and graphite fluoride, with densities of 4.8 to 7.8 g cm^{-3}, were used to control the shock temperature rise and to quench efficiently. Spectroscopic graphite gave the maximum yield of diamond (8%). Chaoite was also observed in the shocked amorphous carbon and glassy carbon. A local temperature rise during shock was inferred from the temperature of some spherical particles, indicative of superheating of the particles to near or above the melting point.

1. Introduction

In 1961, DeCarli and Jamieson [1] recovered diamond from explosively shocked samples of spectroscopically pure artificial graphite at pressures estimated at 30 GPa. Graphite of densities lower than 2.2 g cm^{-3} has been found to exhibit a break in their pressure–volume curves around 23 GPa [2]. Hugoniot measurements on graphites with various crystallographic orientations and initial densities appear to indicate that the minimum particle velocity required to transform graphite to diamond is about 1.5 km sec^{-1} [2, 3]. This means that the direct transformation of graphite to diamond, even in the case of graphites with densities lower than 2.2 g cm^{-3}, seems to be impossible at a steel-flyer velocity lower than about 3 km sec^{-1} by the free surface velocity approximation. However, in a very short duration (of microsecond order) of shock-wave passing, temperature is another important factor to consider for pressure-induced transformations. Therefore, it will be expected that graphite or carbon-bearing species in a porous medium will reduce the transformation pressure due to the temperature rise during shock compression.

In material syntheses by shock loading, most important are the temperature control and quenching products during or after shock. If we have an appropriate material to control the temperature during shock compression and to quench efficiently, we will be able to make diamonds in a relatively low pressure region of the diamond stability field. The material used in the present study to control the temperature is a copper powder for which the Hugoniots have been investigated in detail [4]. Temperature rises by shock compression have been calculated for porous copper with various densities [5]. Furthermore, copper powder is a proper quenching medium for diamond synthesis [6] and also has a higher shock impedance than graphite powder if copper powder with a density greater than about 5 g cm^{-3} is mixed with the graphite powder.

2. Experimental procedure

Starting materials employed in the present study were spectroscopic graphite, amorphous carbon, glassy carbon and graphite fluoride. The amorphous carbon was obtained from furfural resins by heat treatment at 600° C for 3 h in a nitrogen atmosphere. The composition thus obtained was determined to be (wt %) 92.1 C, 5.1 O_2, 2.5 H_2 and 0.3 N_2 by chemical analysis [7]. The graphite fluoride has a formula $(CF)_n$. These four carbon specimen powders (300 mesh) were thoroughly mixed with a pure copper powder (300 mesh). The mass ratio of the carbon specimen to the copper was 4:96.

The mixtures were pressed into stainless steel (SUS 304) capsules, shown in Fig. 1, with an outer dimension of 24 mm diameter and 30 mm length and sample space 12 mm diameter × 4 mm length, at appropriate pressures of 170 to 800 MPa. In the case of mixtures of amorphous carbon and copper the bulk density range was 4.9 to 7.8 g cm^{-3}. The mixtures spectroscopic graphite–copper, glassy carbon–copper and graphite fluoride–copper were pressed at a pressure of 350 MPa, with densities of 7.0 ± 0.2, 6.0 and 7.2 g cm^{-3}, respectively.

A recovery system, as shown in Fig. 1, prevented the capsule from being destroyed by shocks. Shock-recovery experiments were conducted with a 30 mm bore propellant gun, recently installed at the National Institute for Research in Inorganic Materials, for the projectile velocity range 0.655 to 1.88 km sec^{-1}. The projectile velocity was measured by a magnetoflyer method [8]. The capsule was impacted by a 2 mm thick flyer plate made of stainless steel, glued on to the front surface of a high density polyethylene sabot. The total weight of the projectile was 48.5 ± 0.3 g.

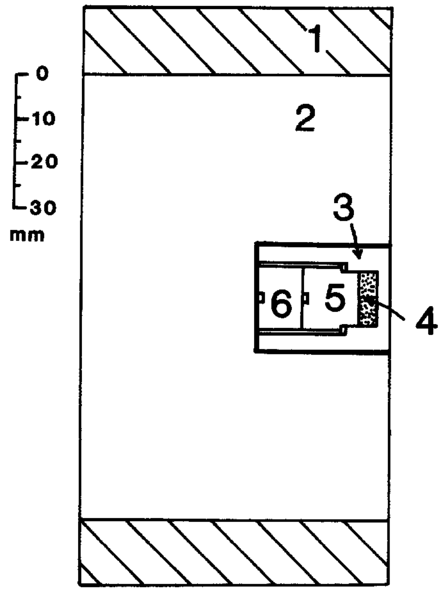

Figure 1 Diagram showing the shock-recovery assembly used in the present study, (1) Supporting ring, (2) capsule holder, (3) capsule (SUS 304), (4) sample, (5, 6) screw caps (SUS 304).

The pressure was estimated from the measured projectile velocity using the impedance match method and the free surface velocity approximation. The final shock pressure might have been increased to some extent by multiple shock reflections, but judging from the sample thickness, did not reach the pressure obtained in the capsule material. Although the temperature for the specimen mixture containing carbon would differ from that for the copper powder with a corresponding density, only the calculated temperature for copper is used as a rough measure of temperature for the mixture. It has recently been recognized that a drag effect of shock waves by high shock-impedance capsule material and three-dimensional wave reflection may greatly influence the shock pressure and temperature of a powdered sample within a capsule. Further studies [9, 10] will be required to determine the actual shock pressure and temperature.

Recovered capsules were mechanically cut open to take the sample out. The samples were immersed in an HNO_3 solution for more than 24 h to remove the copper completely. Undissolved portions were investigated by X-ray and electron diffraction techniques. In a few runs, the undissolved portions were oxidized by lead oxide at 430° C for 10 h in air to remove graphite and unreacted carbon, and investigated again by means of electron diffraction.

The yield of diamond was estimated from observations under electron diffraction and transmission electron microscopy (TEM) and from the results of the oxidation reaction.

3. Results

The experimental conditions and results are listed in Table I. The phases identified in run products are diamond, graphite, and traces of chaoite and unknown phase(s).

The interplanar spacings obtained from the diamonds are given in Table II. The observed d values indicate that all the diamonds in our products are the hexagonal polymorph (lonsdaleite). As seen in Table II, the electron diffraction of the single crystals is indexed as that of hexagonal diamond along the c-axis. Diffraction from the cubic polymorph could not be positively identified. The lack of d_{101}, d_{102}, d_{103}, d_{201} and d_{203} for hexagonal diamond in the ring diffraction patterns is probably due to weak diffraction.

TABLE I Summary of shock recovery experiments for diamond synthesis

Shot. No.	Flyer velocity (km sec^{-1})	Initial density (g cm^{-3})		Initial pressure (GPa)		Capsule pressure (GPa)	Temperature (° C)	Phases identified¶
		Mixture*	Copper†	Mixture‡	Copper‡			
Amorphous carbon								
S 20	0.834	5.87	7.2	6	11	18.0	550 to 750	G + D
S 14	0.98	5.65	7.1	9	13	20.5	700 to 1200	G + D
S 08	0.99	6.78	7.7	12	15	20.8	500 to 800	G + D + X
S 06	1.24	4.87	5.9	10	13	27.0	1400 to 2200	G + D (< 1%) + C + X
S 09	1.22	6.13	7.3	14	18	26.5	800 to 1300	G + D (2%)
S 01	1.24	7.8	8.3	20	23	27.0	450 to 650	G + D + C + X
Spectroscopic graphite								
S 21	0.655	6.78	7.1	7	8	13.5	500 to 550	G + D
S 11	0.99	7.20	7.2	13	13	20.8	650	G + D
S 04	1.25	7.03	7.2	17	18	28.3	900 to 950	G + D (8%)
S 16	1.64	7.00	7.2	25	26	37.0	1250 to 1350	G + D
S 12	1.88	7.10	7.2	32	33	44.0	1650	G + D
Glassy carbon								
S 02	1.24	6.0	7.2	15	18	27.0		G + D (< 1%) + C + X
Graphite fluorite								
S 03	1.24	7.2	7.2	15	18	27.0		G + D (< 1%)

*Calculated from the volume and mass of pressed pellets.

†Estimated on the basis of a calibration curve for the corresponding copper powder, made at the same pressure as for the given mixture.

‡Estimated by the Hugoniots for copper with the initial densities of the mixture and the corresponding copper using the impedance match method. The difference in pressure is at most 2 GPa when he Hugoniots for graphite are taken into account.

§Estimated on the basis of calculations [5] using the initial densities and initial pressures.

¶Parentheses indicate the yield of diamond determined by the oxidation reaction (see text). G = graphite, D = diamond, C = chaoite, X = unknown phase(s).

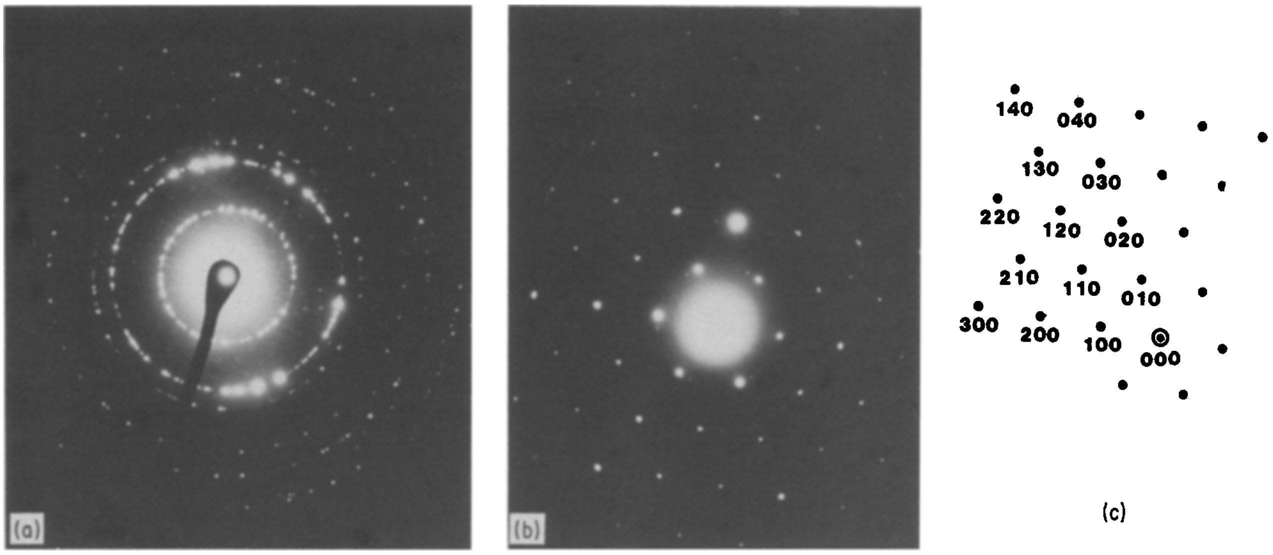

Figure 2 Electron diffraction patterns of diamonds recovered: (a) spotty ring pattern from shocked amorphous carbon, (b) spot pattern from shocked spectroscopic graphite, (c) indexing along the *c*-axis of hexagonal diamond.

Figs 2a and b illustrate typical electron diffraction patterns for the diamond obtained in our procedure. In the course of electron diffraction and TEM observations, two shapes of single crystals of diamond were found in several runs. One is of rounded shape (Fig. 3a) and the other is a thin plate. Most of the diamonds were aggregates of small crystals (less than 0.1 μm). The yields of diamond determined by the oxidation reaction are listed in Table I. The results of electron diffraction and TEM observations indicate that the yield is not significantly dependent on the estimated pressure within the pressure range investigated, and that it decreases slightly with decreasing initial density.

Most graphite grains have irregular shapes. Some have spherical shapes (Fig. 3c) and occasionally sheared-grain structures (Fig. 3b). In general, the amount of spherical shapes increased with increasing pressure. A single crystal of chaoite also was identified from the shocked amorphous carbon and glassy carbon, but not from the shocked spectroscopic graphite and graphite fluoride. The formation of chaoite appears to depend not upon the calculated. temperature, but rather upon the form of the starting carbon. Our TEM study was not successful in identifying chaoite grains, probably because of their small size and number.

The calculated temperature for copper indicates a range of 450 to 2200° C for the amorphous carbon–copper mixture and 500 to 1600° C for spectroscopic graphite–copper. For the lower density mixtures, the calculated temperature gives a large range and higher values. They are still below the melting temperature of carbon and in the stability field of diamond, as shown in Fig. 4. However, the spherical shape of the particles indicates their formation at quite high temperatures near or above the melting point. They distribute evenly in the low temperature and low pressure sample of Shot No. S21 (Table I) and the amount increases with increasing pressure. This is suggestive of a local temperature rise in the sample, especially in the carbon. It is likely that the temperature of the carbon during shock compression is higher than that in the surrounding copper.

TABLE II Electron diffraction data for shock-recovered diamonds

hkl	Values reported for hexagonal diamond				Values of *d* (nm) for observed diamond					
	Bundy and Kasper [11] (a = 0.252 nm, c = 0.412nm)		Frondel and Martin [12] (a = 0.251 nm, c = 0.412 nm)		S 20 (spot)	S 08 (spot)	S 01 (spot)	S 21 (ring)	S 11 (spot)	S 04 (spot)
	d (nm)	*I*	*d* (nm)	*I*						
100	0.219	s	0.218	4	0.217	0.217	0.217	0.217	0.217	0.218
002	0.206*	s	0.2061	10				0.206		
101	0.192	m	0.1933	2						
102	0.150	w	0.150	1						
110	0.126*	ms	0.1257	6	0.125	0.127	0.124	0.125	0.126	0.127
103	0.117	m	0.117	1						
200	0.109	–			0.108	0.109	0.108		0.109	0.110
112	0.1075*	m	0.1075	3				0.108		
201	0.1055	w								
203	0.855	w								
210	0.0826	w			0.0823	0.0821	0.0817	0.0813	0.0821	
300	0.7208†	–			0.0719	0.0726	0.0726		0.0720	0.0722

*Reflections coincident with or overlapped by those of cubic phase of diamond.
†Calculated.

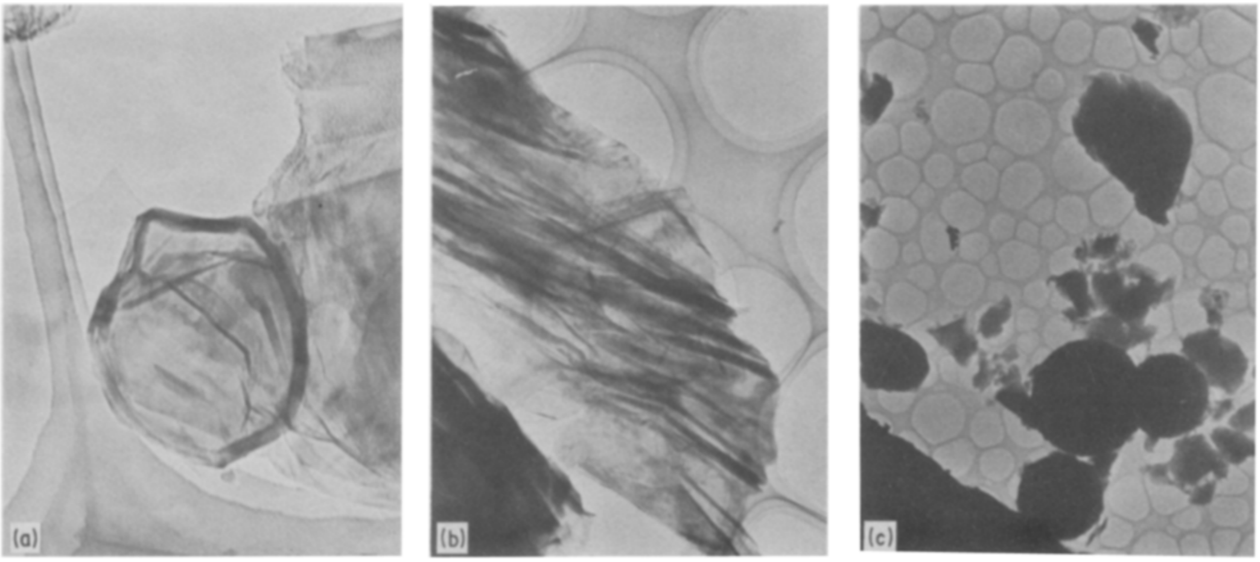

Figure 3 TEM observations of diamond and graphites from shocked spectroscopic graphite: (a) rounded grain of diamond with approximate diameter 0.5 μm, (b) graphite grain showing sheared structure (view 6.7 μm × 9.2 μm), (c) spherical particles quenched from liquid state. The largest diameter is about 1 μm.

4. Discussion

Our results indicate that all the samples subjected to weak shock loading contain the hexagonal form of diamond. This is not dependent upon the starting carbon form, at least for the four used in the present study. The hexagonal form of diamond was first synthesized by Bundy and Kasper [11], and found in meteorites [12, 13], placers [14], eclogite [15], and synthetic diamond in shocked well-oriented graphite [6]. The shock-recovered sample of full-density graphite at 100 GPa produced cubic and hexagonal diamonds in an iron matrix and only cubic diamond in the mixture with copper [16, 17].

The mechanism for diamond formation by shock compression has not yet been settled [18]. De Carli and Jamieson [1] proposed a diffusionless, *c*-axis compression of rhombohedral graphite present in the starting graphite. De Carli [19] suggested a two-step process to explain subsequent experimental results. A diffusionless collapse of graphite to a glass-like tetrahedrally bonded structure occurs in the first step and is then followed by continuous recrystallization, even after the pressure drop into the stability field of graphite. Thereafter, De Carli [20] formulated a nucleation and growth mechanism, consistent both with the experimental data and calculations using fundamental conservation laws. According to this model, his calculation indicates that about 15 and 27% of the starting ATJ graphite will be heated up to 3500 K at about 15 and 25 GPa, respectively. De Carli's recovery experiments indicate that these calculated percentages correspond to the amounts of diamond formed by shock compressions to 15 and 25 GPa, respectively. Setaka and Sekikawa [7] synthesized cubic diamond from amorphous carbon by explosive shocks at 60 to 100 GPa. They proposed a crystallization process of cubic diamond from the liquid state during shock. Meteoritic diamonds are also proposed to have formed via a liquid carbon intermediate, rather than by direct, solid-state transformation of graphite [21]. Trefilov *et al.* [22] have synthesized cubic diamond in a relatively low pressure region by raising the temperature to 4000 to 4500 K, near the triple point, to enhance the direct graphite–diamond transition during shock passage.

Judging from these observations, the hexagonal form of diamond obtained in the present study elucidates two points. First, there exists an intermediate

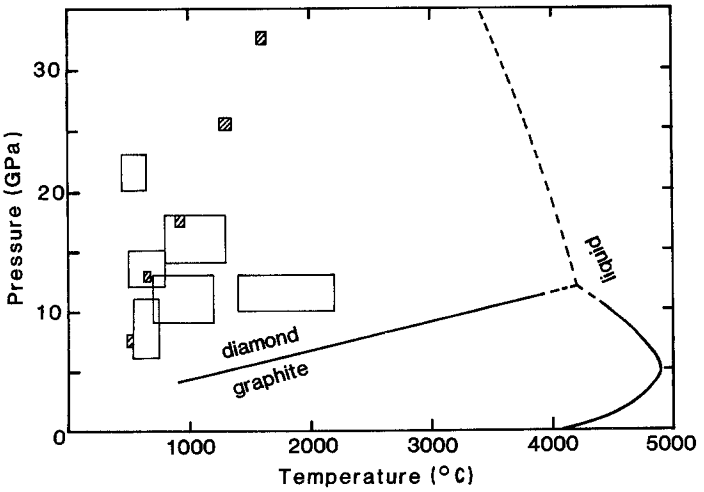

Figure 4 $P-T$ diagram showing estimated experimental conditions for amorphous carbon (open rectangles) and spectroscopic graphite (shaded rectangles), together with phase boundaries for graphite, diamond and liquid (after Bundy [26]).

temperature condition during weak shock where the temperature is not so low that the starting carbon remains in its graphite form but not so high that only cubic diamond forms. Secondly, diamond can be synthesized by a relatively weak shock loading with temperature control. The transformation mechanism might be explained by a martensitic reaction.

There is another problem related to the quenching products after shock passage. Trueb [16] investigated the relationship between the particle size of diamond and the proportion of hexagonal diamond formed, by measuring X-ray diffraction peak heights. He found that the particle size range decreases rapidly with increasing content of hexagonal diamond. His explanation is that hexagonal diamond formation is not favoured by high temperature and that the smaller particles are quenched more efficiently than the larger ones. The former is consistent with the static synthetic data [11] and our present results. The latter implies that relatively large grains of cubic diamond may be quenched by strongly shocked graphites or by weakly shocked graphites under pre-superheated conditions. This is also consistent with experimental data [22].

Traces of chaoite were observed in the shocked amorphous carbon and glassy carbon (Table I). Glassy carbon explosively shocked at 100 GPa contained chaoite as well as cubic diamond [23]. Excellent reviews on carbyne phases have been published [24, 25]. According to one proposal [24], the formation region of carbynes is surrounded by graphite, diamond, liquid and vapour phases in the pressure–temperature diagram. However, this is still preliminary and remains open to question. The electron diffraction patterns of unknown phase(s) do not appear to correspond to any of the diffraction data reported as carbon phases. A detailed investigation is currently under way.

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