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Diamond formation from glassy carbon under high pressure and temperature conditions

SHIN-ICHI HIRANO, KAZUAKI SHIMONO, SHIGEHARU NAKA
Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Furo-cho, Chikusaku, Nagoya 464, Japan

The process of the formation of diamond from the glassy carbon with its characteristic bond nature was investigated in the diamond stable region at high pressures (up to 10 GPa) and temperatures (up to 3000° C), without any intentional addition of metals as solvent. The process of diamond formation was found to obey Ostwalds's step rule as follows: amorphous glassy carbon crystallized to form fully well-crystallized graphite prior to diamond formation and then the graphite crystals were converted to diamond by further heat treatment at pressures above 9 GPa. The many trigons formed are considered to be essentially a record of growth failure in the growth period. As a result of heat treatment for a longer time and/or at a higher temperature close to the diamond–graphite stability boundary, the diamond tended to grow with the (1 1 1)-face composed of the thin growth layers.

1. Introduction

Extensive researches have been carried out on synthetic diamond formation since the first substantiated synthesis of diamond was announced in 1955 by Bundy *et al.* [1]. Three successful techniques for the synthesis have been proven.

The first method, mainly used for industrial diamond production, is the dissolution and crystallization process using a metal solvent under relatively static high pressures and high temperatures.

The second method is a direct transformation of graphite to diamond by explosive shock-wave compression, reported by DeCarli and Jamieson [2]. They transformed graphite to diamond in the order of a few microseconds under a pressure of 30 to 40 GPa at about 1125° C. Alder and Christian [3] also found evidence that graphite, compressed and heated by a strong shock-wave to about 35 GPa and 725° C, converted to diamond. Bundy [4] first reported the direct conversion of graphite to diamond under the static pressure, using an electric flash-heating technique under pressures above about 12 GPa.

A third process has been reported by Eversole [5]. The spiral growth of diamond was found to occur, in the metastable region of diamond, as epitaxial thin film on diamond substrates by the relatively high-temperature solid–gas reactions under surprisingly low pressures, for instance at 1000° C and less than 900 MPa.

Wentorf [6] exposed several different forms of elemental carbon and a number of organic compounds to pressures in the range 9.5 to 15.0 GPa and temperatures in the range 1300 to 3000° C for periods of 0.2 to 50 min, and found that the amount and kind of diamond formed depended strongly on the kind of carbonaceous starting material used. This fact is conjectured to suggest that structural factors of the starting carbonaceous material are involved, and that the actual transformation to diamond may follow a number of complex paths.

Although the production of diamond has been commercially realized, mainly using the metal-solvent method, and many observations have revealed the characteristics of the synthesized diamonds, after the work by Tolansky and Sunagawa [7], a clear understanding of the behaviour of carbonaceous materials and the process of diamond formation without any metal solvent in the stable-diamond region are still the

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subject of discussion. This paper describes the results of experiments in which glassy carbons with the characteristic diamond bond nature were exposed to pressures of up to 10 GPa and temperatures of up to 3000° C in the stable-diamond region without any intentional addition of metals as the solvent. Microscopic observations on the transformation of the glassy carbon to diamond through the well-crystallized graphite of a metastable phase are also described.

2. Experimental procedure

The glassy carbons used were the highly pure powders GC-20 and GC-30S (from Tokai Carbon Co. Ltd.) with grain sizes in the range 200 to 350 mesh, preheat-treated at 1850° C and 2950° C, respectively. The total metallic impurity content amounted to a few parts per ten thousand. The powder sample of weight 90 mg was placed in the sample cell arrangement, as shown in Fig. 1, and then subjected to a desired pressure of up to 10 GPa in a girdle-type high-pressure apparatus. The sample was heat treated by passing a 60 Hz alternating current directly through it, and quenched to room temperature under pressure. The experimental procedure was basically the same as that reported by Naka *et al.* [8].

The pressure on the sample was calibrated at room temperature in the ordinary way by detecting the changes in the electrical resistances associated with the polymorphic transitions of reference metals [9, 10]. The temperature of the sample was determined with a chromel–alumel thermocouple, inserted in the central part of the cell, measuring temperatures of up to about 1000° C. The melting points of Ag and Au embedded in the central part of the sample were also used as fixed points for the determination of the temperature with the applied electric power under pressures of 4, 6, 9 and 10 GPa, being calibrated against the pressure effect by Cohen *et al.* [11] and Strong and Bundy [12]. The pressures and temperatures reported here may be in absolute error by as much as 10% and in relative error by about 5%.

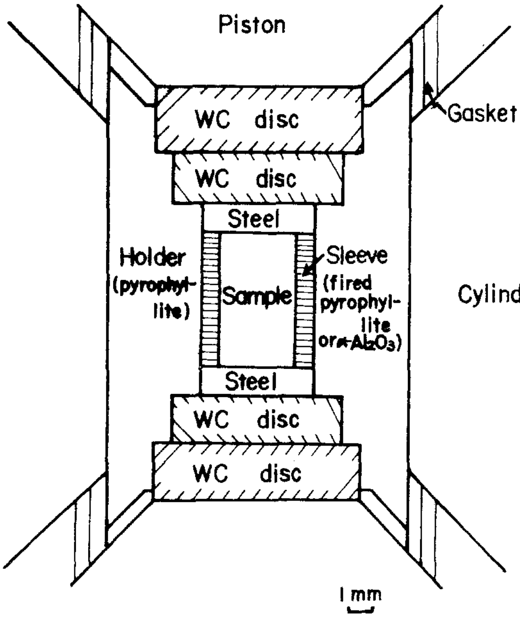

Figure 1 Sample cell arrangement.

The specimens heat treated under pressure were identified by the X-ray diffraction method and observed under a scanning electron microscope. Two kinds of profiles of the 002 X-ray diffraction line of graphite were observed on the specimens heat treated under pressure. One is symmetrical after correction to the diffraction intensities for the Lorentz-polarization, atomic scattering and absorption factors. The other is the so-called "composite profile" which indicates the coexistence of the turbostratic structure, as in the original glassy carbon and the graphitic structure formed. The composite profiles were graphically separated into two symmetrical component profiles corresponding to each structure by the conventional method reported by Hirano [13] and Noda *et al.* [14]. The amount of graphite formed from the glassy carbon was measured as the area ratio of the profile for the graphitic component to the composite profile after the correction for the preferred orientation of crystallite. The 004 X-ray diffraction profile of graphite hardly appeared by the deformation of graphite on treating at high pressure and temperature during diamond formation.

3. Results and discussion

It was found that the glassy carbon of the turbostratic structure bonded with the criss-cross linkage could not be transformed directly to the diamond by the heat treatment under static pressure in the stable-diamond region, but converted to the diamond through the well-crystallized graphite of the metastable phase. The graphite crystals with the same c_0-spacings of 0.6708 nm as the natural graphite formed from GC-20, even at temperatures as low as 600° C under 4 GPa. Diamond formation did not take place by treat-

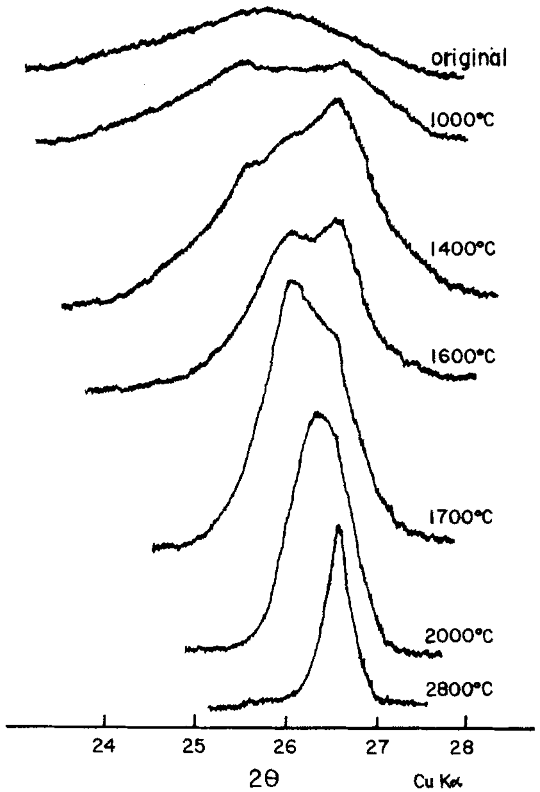

Figure 2 Observed X-ray diffraction profiles on specimens treated at various temperatures under 9 GPa for 5 min.

ments at temperatures up to 2800° C under 4 and 6 GPa, but occurred after 5 min at 2300° C under 9 GPa and at 1800° C under 10 GPa.

Fig. 2 shows the observed 002 X-ray diffraction profiles of the specimen treated at various temperatures less than 9 GPa for 5 min. The X-ray diffraction profile became to be so-called "composite" as the amorphous glassy carbon had been crystallized to the graphite crystal, being shown on the profile at 1000° C. The c_0-spacing of the graphite crystal thus formed was 0.6708 nm, the same value as that of natural graphite. The higher the heat-treatment temperature, the more the amount of the graphite formed, up to 2200° C.

Fig. 3 illustrates the process of diamond formation through the metastable graphite from the glassy carbon GC-20 under pressure of 9 GPa. Graphite formation (G in Fig. 3) increased up to 2200° C with increase in the heat-treatment temperature, and then gradually decreased, followed by diamond formation (D in Fig. 3) as the stable crystalline phase with further heat treatment under the pressure. It is seen that the diamond formation (D in Fig. 3) from the amorphous carbon (A in Fig. 3) like a glassy carbon, obeys Ostwald's step rule characteristic of the contribution of the intermediate metastable phase (G) on transformation.

Fig. 4 shows a feature of the process of diamond formation from the amorphous glassy carbon under a pressure of 9 GPa. Prior to diamond formation, the original glassy carbon grains of GC-20 of irregular shape (like pieces of broken glass) (Fig. 4a) transformed to the well-crystallized graphitic crystal of preferred orientation of graphite layers, as shown in Fig. 4b, by heat treatment at 2200° C under 9 GPa for 5 min. Fig. 4c demonstrates the transition state showing the manner in which crystals formed on a graphite crystal

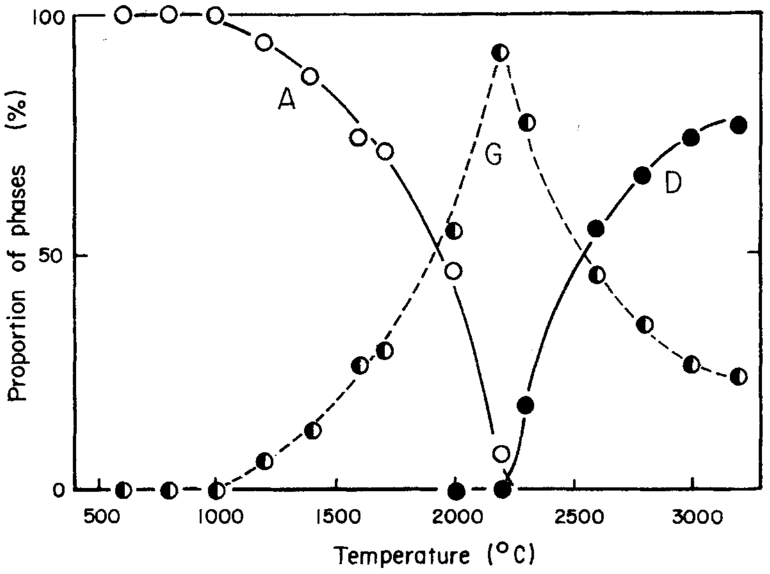

Figure 3 Changes in the amounts of phases of amorphous glassy carbon (○), crystallized graphite (◐) and formed diamond (●) under 9 GPa on GC-20: (A) amorphous glassy carbon; (G) graphite; and (D) diamond.

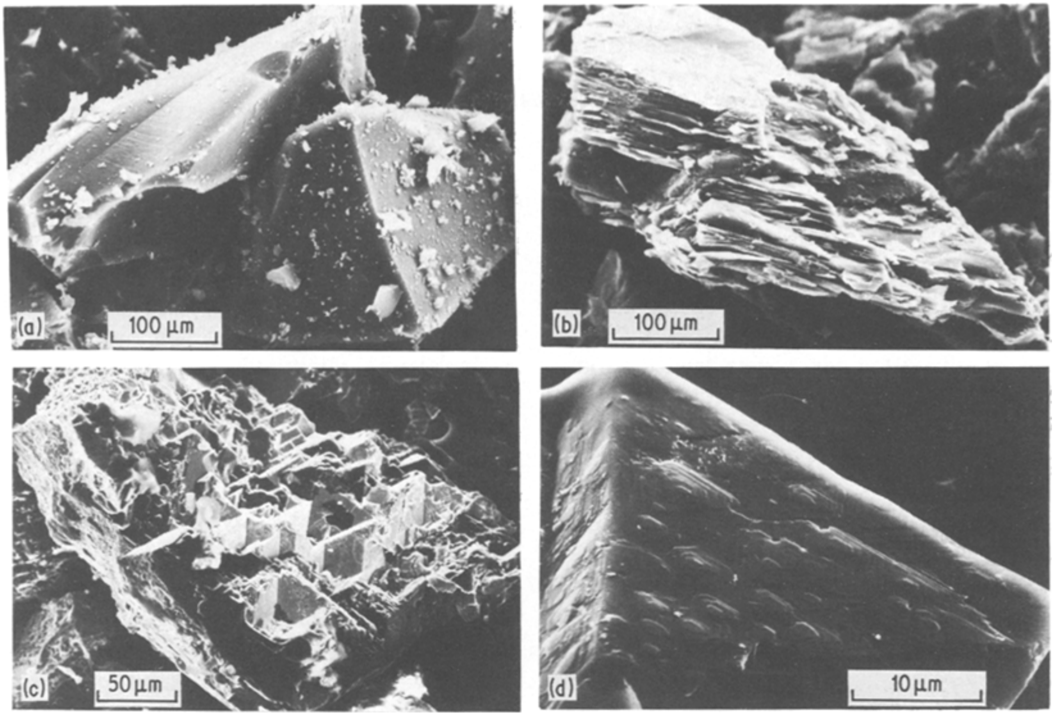

Figure 4 Feature of the process of diamond formation from GC-20 under 9 GPa. (a) Original GC-20 powder, (b) crystallized graphite crystal with preferred orientation of layer as metastable phase at 2200° C, (c) diamond crystals formed on graphitized grain at 2800° C and (d) surface microtopograph of diamond (1 1 1) face formed at 2800° C.

grain. The diamond crystals nucleated on the graphite grain (at the lower part of the grain in Fig. 4c) to grow gregariously in the octahedral form along the direction restricted by geometrical selection. At higher temperatures, for example, 2800° C, the developed (1 1 1) diamond surface also tended to be covered with the thin growth layers composed of several growth hillocks, as shown in Fig. 4d.

On the (1 1 1) diamond face many trigons in the same orientation were observed to originate in some way intimately connected with the growth failure on the (1 1 1) plane. The process of diamond formation at pressures less than 10 GPa was found to be exactly the same as that at pressures less than 9 GPa. Fig. 5 shows evidence of the survival of the trigons during growth. Similar features were also experimentally observed, as shown in Fig. 6, on the specimen treated at 3200° C under 9 GPa in which diamonds had grown very rapidly. The origin of the trigons has been the subject of much dicussion. Tolansky and Wilcock

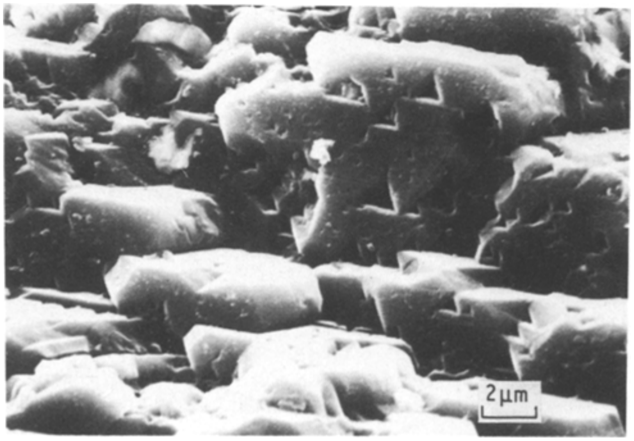

Figure 5 Trigons on diamond (1 1 1) face formed at 2400° C under 10 GPa.

[15], Helperin [16, 17], Tolansky and Sunagawa [18] and Varma [19–21] conceived trigons to have originated in growth, whereas Omar and Kenawi [22], Frank *et al.* [23], Frank and Puttick [24], Wilks [25], Patel and Ramanathan [26], Patel *et al.* [27] and Lang [28] explained them as due to etching (dissolution). It follows from the present results that trigons might be essentially a record of the growth failure. With prolonged heat treatment and/or treatment at higher temperatures, close to the diamond–graphite stability boundary, the diamond crystals tended to grow with the development of the (111) face of the typical surface microtopograph, as shown in Fig. 7. It would appear that the trigons were retained due to the failure in growth and then the mobile carbon species might partly contribute to complete the relatively smooth (111) diamond face in an opening formed due to the spacial reduction on the transformation to diamond (density, $d = 3.51\,\mathrm{g\,cm^{-3}}$) from graphite ($d = 2.26\,\mathrm{g\,cm^{-3}}$).

As the reference experiment, the glassy carbon GC-20 and powder samples of mixture 20 wt% electro-deposited pure iron and 80 wt% glassy carbon were heat treated at 9 GPa with Mo-metal, instead of a steel disc, in the pressure cell, in order to examine the effect of iron diffusing from the steel end-discs. As for the glassy carbon, GC-20 itself, the well-crystallized graphite was formed at 1200° C and the amount of the graphitized grains increased with increasing heat-treatment temperature. At about 2100° C the electric current passing through the sample became unstable, resulting in decrease of the electric current, probably due to the formation of molybdenum carbide, which made the performance of the experiment at higher temperatures difficult. Diamond formation could not be observed up to about 2100° C, but the formation of the well-crystallized graphite as the metastable phase was confirmed, in a similar way as that shown in Fig. 3.

The glassy carbon of GC-30S preheat-treated at 2950° C did behave in the same way as GC-20, except that the higher temperature was required for the growth of the well-crystallized graphite crystals. Diamond formation was also found not to take place prior to the graphite formation with a similar crystallinity to the natural graphite as the metastable phase.

These results indicate that the characteristic chemical sp^3-bond of the criss-cross linkage found in the initial glassy carbon did not act as the nucleation site for diamond formation under the static pressure, but was broken down to form the graphitic structure with sp^2-bond nature. In the present work, the diamond crystals were all covered with the (111) faces which were directly bonded with neighbouring diamond grains because the temperature and pressure condition for the diamond formation was high enough to form the direct bonds among the formed diamond grains. The present method for the diamond formation with glassy carbon is expected to be applicable for the production of the sintered body of diamond with the preferred orientation of the (111) face.

4. Conclusions

Glassy carbon is a typical non-graphitizable carbon, having the turbostratic structure.

The glassy carbons used were highly-pure powders, of GC-20 and GC-30S (from Tokai Carbon Co. Ltd) preheat-treated at 1850 and 2950° C, respectively. The heat treatments were

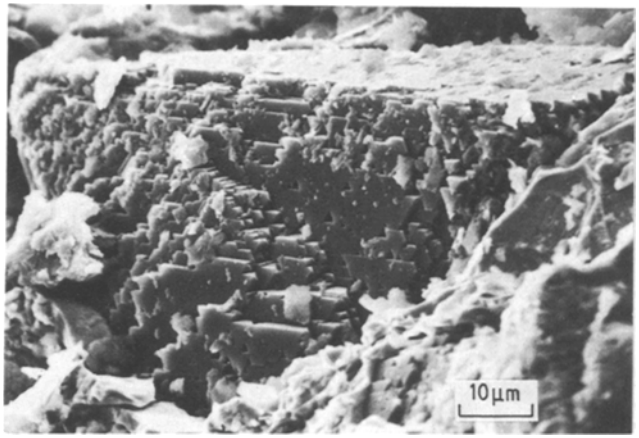

Figure 6 Characteristic formation of trigons on diamond formed at 3200° C under 9 GPa for 5 min.

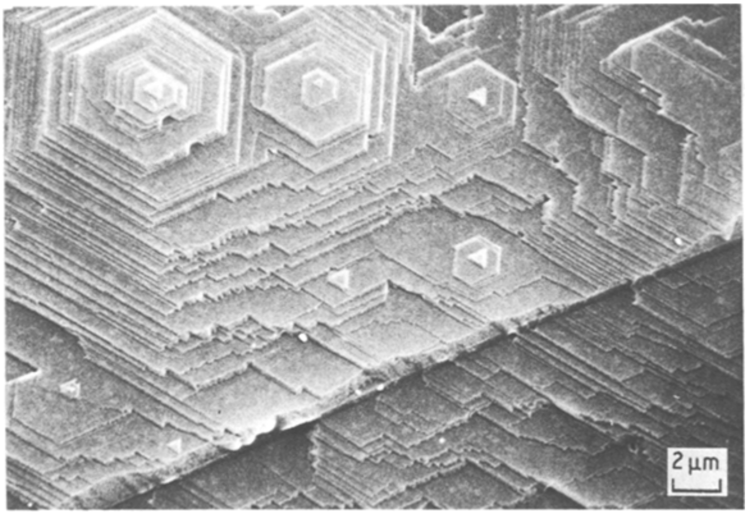

Figure 7 Characteristic surface microtopograph of (1 1 1) face of diamond crystal grown at 2600° C for 15 min under 10 GPa.

carried out by passing alternating electric current directly through the powder sample compressed at pressures of up to 10 GPa.

It was found that glassy carbon could not be transformed directly to diamond by heat treatment under static pressure in the stable-diamond region, but was instead converted to diamond from well-crystallized graphite, formed after further heat treatment at the same pressures above 9 GPa. Graphite crystals with the same c_0-spacing of 0.6708 nm as natural graphite were formed, even at temperatures and pressures as low as 600° C and 4 GPa. Diamond formation was not observed to result from treatment at 6 GPa, but was observed to take place after 5 min at 2300° C and 9 GPa and after 5 min at 1800° C and 10 GPa.

Many trigons were observed in the diamond crystals formed at less agressive conditions, for example, below 2600° C 10 GPa for 5 min. After heat treatment for a longer time and/or at a higher temperature, close to the diamond–graphite stability boundary, the diamond crystals tended to grow with (1 1 1) faces composed of a thin hexagonal growth layer.

Diamond formation was found not to occur unless the graphite crystals with crystallinity similar to the natural graphite were formed as the metastable phase.

These results indicate that the characteristic chemical sp^3-bond in the glassy carbon did not act as the nucleation site for diamond formation under static pressure, but instead was broken down to form the graphitic structure with sp^2-bond nature.

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