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DIAMOND SYNTHESIS: OBSERVATIONS ON THE MECHANISM OF FORMATION

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ABSTRACT

A brief history of diamond synthesis, as well as instrumentation capable of accomplishing the experiment, are given. The direct conversion of graphite to diamond by severe transient pressure and high adiabatic temperature is reviewed. Current tentative explanations of the mechanism are discussed. Studies performed at the U. S. Army Electronics Research and Development Laboratory on several metal-carbon, metal-carbon-silicate, and carbon-nonmetallic salt systems are described and data presented. A mechanism of formation is proposed for synthesis performed under relatively static high pressures and high temperatures; namely, crystallization from solution. Supporting evidence is given. The use of secondary chemical reactions in diamond formation processes also is described. A brief discussion is presented on correlation of laboratory data with the genesis of natural diamond.

INTRODUCTION

The first serious attempt by man to create diamond occurred approximately 80 years ago (Hannay, 1880). A second venture was reported 14 years later by Moissan (1894). The first substantiated synthesis was announced in February of 1955 by the General Electric Company Research Laboratory, Schenectady, N. Y. (Bundy *et al.*, 1955). Shortly thereafter, a second success was reported by the Swedish firm of Allmänna Svenska Elektriska Aktiebolaget (1955). Data on the third independent synthesis, by the U. S. Army Electronic Research and Development Laboratory, was published 5 years later (Giardini *et al.*, 1960). Within a few years, therefore, this significant mineral which withstood duplication for so long, became a routinely producible material.

Although the production of diamond has been reduced to practice, a clear understanding of the mechanisms of formation still is subject to discussion. Thus far two distinct thermodynamically permissible physical-chemical techniques have proven successful. The first, used by all references cited above, essentially involves a reaction of carbon with an intermediate material under relatively static high pressures and high temperatures. The second method, first announced by the Stanford Research Institute of Menlo Park, California (DeCarli and Jamieson, 1960), constitutes a direct transformation of graphite to diamond. The latter is accomplished by subjecting graphite to a very high instantaneous stress developed by explosive shock.

A third process has been recently reported by the Union Carbide Corporation of Kenmore, N. Y. (Eversole, 1962). Relatively high temperature solid-gas reactions are carried out at surprisingly low pressures.

Diamond growth is reported to occur as epitaxial thin films on diamond substrates.

Instrumentation

Thus far, with the exception of the epitaxial film process, concurrent pressures and temperatures of at least 45 kilobars[1] and 1150° C., respectively, have been found necessary to effect diamond growth. Figure 1 provides a schematic summary of the principal types of instruments which have proven capable of primary diamond synthesis.

Figure 1(a) illustrates the now famous "Belt" high pressure-high temperature apparatus of the General Electric Company (Hall, 1960). This type of device produced the first synthetic diamond. It is still one of the most effective pressure vessels available today. Its principal design feature for generating high pressures is the compressible preformed conical gasket.

Figure 1(b) shows a cross sectional schematic of the "Supported Stepped Piston-Cylinder" chamber of the U. S. Army Electronic Research and Development Laboratory (Giardini and Tydings, 1959 and 1961). This device is capable of generating sustained pressures and temperatures to 100 kilobars and 2500° C., respectively. It has been used for most of the work on diamond reported herein.

Figure 1(c) provides a perspective schematic of H. T. Hall's "Multi-Anvil" pressure apparatus of tetrahedral configuration (Hall, 1958). This device normally functions on the principle of an extruded compressible gasket. It recently has been observed, however, that preformed compressible gaskets provide superior performance.[2] Sample deformation normally encountered is markedly reduced because of the diminished displacement of compressible solid from the pressure cavity.

Figure 1(d) presents a cross section of the "Girdle" chamber developed by the Battelle Memorial Institute (Wilson, 1960). Although similar to the "Belt" in geometrical appearance, this device utilizes the elasticity of multiple steel binding rings in place of the compressible gasket principle.

Figure 1(e) illustrates the "Multi-Anvil" device of cubic configuration first used by Allmänna Svenska Elektriska Aktiebolaget (Liander and Lundblad, 1960), and recently developed into a self-contained unit by Barogenics, Inc. (Zeitlin *et al.*, 1961). A structural framework supports and directs six centrally converging hydraulically powered anvils oriented

[1] 1 bar $=1.0197$ kg/cm$^2=0.9869$ atmospheres $=14.5038$ psi. $=1\times10^6$ dynes/cm^2.

[2] Based on work conducted at this laboratory with 2000 ton force capacity multi-anvil devices. Preformed gaskets should be an integral part of the compressible solid workpiece rather than attached thereto.

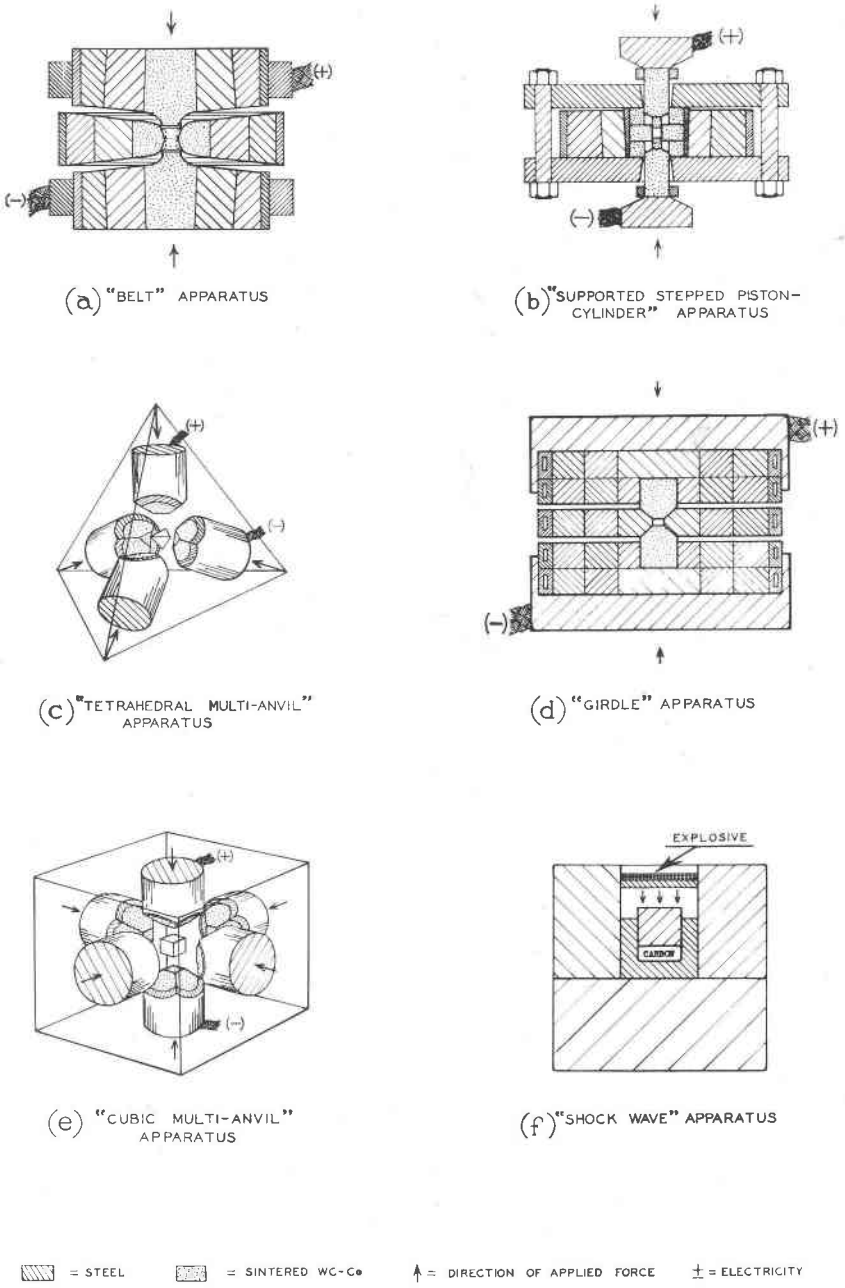

FIG. 1. A schematic summary of high pressure-high temperature apparatus capable of synthesizing diamond.

90 degrees to each other. This unit also operates on the principle of an extruded compressible gasket, although preformed gaskets similarly have been found to provide superior characteristics (see footnote[2] on page 1394).

Figure 1(f) constitutes a cross sectional schematic of the explosive shock apparatus developed by the Stanford Research Institute (De Carli, 1962). A "shaped" explosive charge is detonated against a free piston so as to direct a planar shock wave into a solid cylindrical specimen. Pressures and temperatures, determined to be of the order of 400 to 500 kilobars and 1000 to 1500° C., respectively, have been generated for intervals of approximately one micro-second. Graphite has been successfully converted directly to diamond with this device.

Thermodynamics of Diamond Formation

The chemical thermodynamics of the carbon-carbon system (hexagonal graphite-cubic diamond) have been studied in detail by Rossini and Jessup (1938) and by Berman and Simon (1955). Although both forms of carbon exist in nature, only graphite is truly stable. Diamond may be classed as metastable, as its rate of reversion is imperceptible under normal conditions, and measurable only at temperatures in the vicinity of 1000° C.

The relationship,

$$C_{graphite} \rightleftharpoons C_{diamond}$$

discussed in terms of free energy, yields

$$F_d - F_g = \Delta F.$$

It is common knowledge that a negative value of the relative free energy, ΔF, signifies permissibility for the above carbon-carbon reaction to proceed to the right. Under such conditions the diamond crystal structure would be a stable one. Conversely, a positive value designates that left is the only permissible direction of net change, thus specifying graphite as the stable structure. A zero value of ΔF represents no net change, a permissible coexistence of both graphite and diamond, and therefore, a state of equilibrium. The kinetics of change are not considered here. The latter has been discussed by both A. Neuhaus (1954) and H. T. Hall (1956). Additional work is to be done in this area of diamond synthesis.

Values of ΔF calculated from experimental data taken at normal pressure are positive to approximately 1200° C. (Berman and Simon, 1955). Graphite, consequently, is the phase which might be expected from any formative process carried out under normal pressure. In order to establish the permissibility for possible diamond formation, some environmental

change must be imposed on the system in order to create a favorable balance of energy. The relationship,

$$\int_{o}^{P} \Delta V dP = \Delta F_{TP} - \Delta F_{T^0}$$

with ΔV a function of both P and T, shows that ΔF can be made negative by increasing pressure. A plot of $\Delta F = 0$ as a function of pressure and temperature, as determined by Berman and Simon (1955), is included in Figs. 9 and 10. The region of diamond stability (ΔF = negative) lies above the equilibrium line of $\Delta F = 0$. It can be seen that theory postulated high pressure as a requisite for diamond synthesis. Thus far all experimentation with the exception of the epitaxial growth process of Eversole (1962) has proven this prediction to be correct.

Growth Mechanisms

Direct conversion

Since the method used by the Stanford group for diamond formation is the most direct, it will be discussed first. The apparatus used has already been reviewed in the section on instrumentation. Graphite is placed within a hollow right circular cylinder of stainless steel closed at one end and plugged at the other with a movable solid stainless steel piston. A planar charge of explosive is detonated so as to direct the resultant shock front along the axis of the piston-cylinder assembly enclosing the graphite. Stress duration is approximately 1 micro-second. At pressure intensities calculated to be between 400 to 500 kilobars, along with resultant adiabatic temperatures estimated at 1000 to 1500° C., a reproducible direct conversion of graphite to diamond has been accomplished.

Both spectrographic and commercial grades of graphite have been successfully transformed to diamond. Although rather large samples may be handled by the shock wave technique, yields realized thus far generally run below 5%. The diamonds crystallized resemble meteoric carbonado, and are found as finely disseminated clusters generally less than 10 microns in size. Their color is black. They are poorly crystallized, yielding a diffuse *x*-ray diffraction pattern. The material appears to possess the hardness characteristic of natural diamond. Figure 2 shows a view of a typical starting plug of graphite and the resultant graphite+diamond reaction product.[1]

Two tentative explanations have been advanced on the mechanism of conversion. The first is based upon the partial similarity in the arrangement of atoms in diamond and the rhombohedral modification of graphite (De Carli and Jamieson, 1960). In contrast to normal hexagonal graphite,

[1] Material provided by Dr. P. De Carli of Stanford Research Institute.

where planes of hexagonally arranged carbon atoms are staggered laterally with respect to the principle axis so that every other layer lies directly above the first, the rhombohedral structure shows three consecutively staggered layers with the third being directly above the first. This yields a relatively close geometrical analogy along the principal axis of rhombohedral graphite compared to the octahedral axis of diamond. A simple compression of approximately 61.5% along the weakly bonded *c*-axis in conjunction with a minor lateral translation of about 0.25 Å,

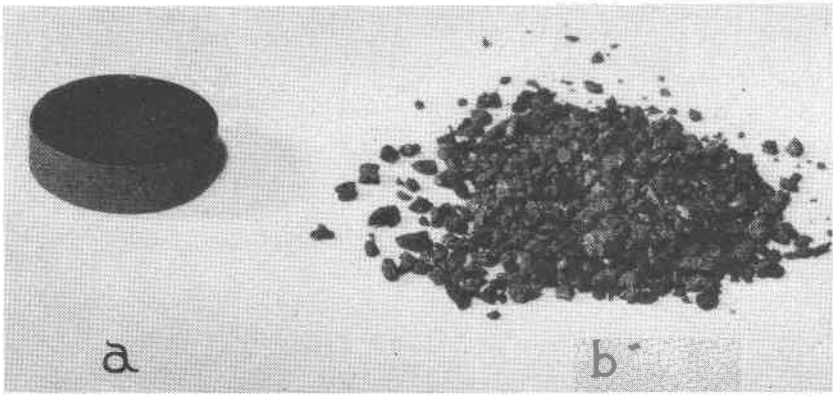

FIG. 2. Example of (a)—A typical graphite specimen prior to shock-induced very high pressure and high temperature, and (b)—graphite plus diamond reaction product subsequently recovered.

brings the atomic positions into proper tetrahedral configuration analogous to that in diamond. The small conversion yield of graphite to diamond roughly corresponds with the usual rhombohedral content of stock graphite.

The second interpretation is simply that of a general disruption of the graphite crystal structure and carbon bonding with subsequent recrystallization at some time during the pressure cycle (De Carli, 1962). During the recrystallization period, random sites experiencing proper bond orientation succeed in crystallizing as diamond. The interpretation of the conversion mechanism is still under discussion.

Crystallization from solution

Although the formation of diamond through reaction of carbon with some intermediate material under essentially static fields of high pressure and temperature has been described as catalytic (Bovenkerk *et al.*, 1959), and catalytic solution (Bundy *et al.*, 1961), it has been the contention of the writers that the process can be satisfactorily described within the

bounds of ordinary chemical solution (Giardini *et al.*, 1960) and (Giardini *et al.*, 1961).

The bulk of the physical-chemical investigation on diamond synthesis conducted at this laboratory has been concerned with metal—carbon systems; primarily reactions of spectrographically pure graphite with the elements Li, Ni, Co, Fe, Mn, Cr, Cu, Pt and Ta (and alloys and mixtures thereof). In addition, studies have been made on systems of metal, carbon and silicates, and also carbon with non-metallic salts such as NH_4Cl,

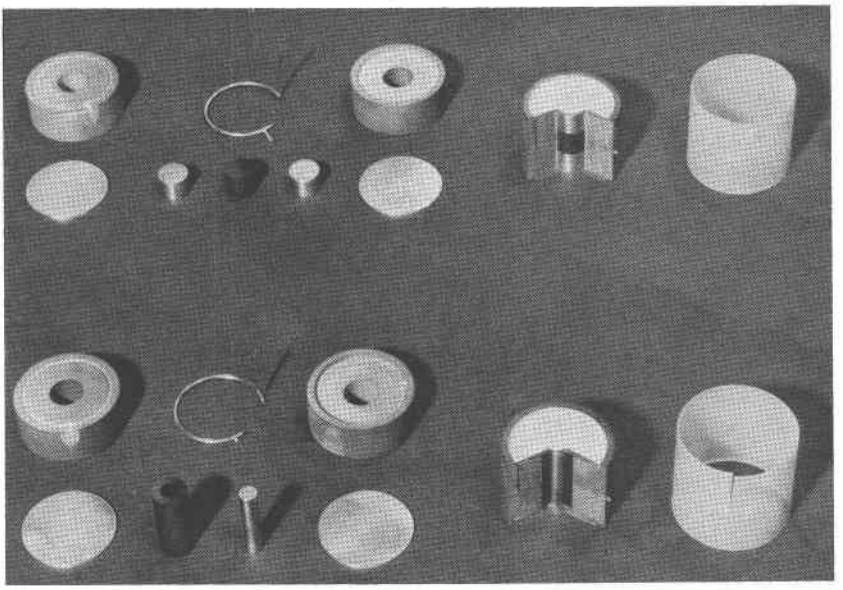

FIG. 3. Typical examples of high pressure-high temperatuve cavity components used for diamond synthesis.

NH_4Br, NH_4I and $(NH_4)_2HPO_4$. The discussion to follow will deal mainly with the first category.

The equipment used for the research is primarily that shown in Fig. 1(b), namely, the Supported Stepped Piston-Cylinder device. Figure 3 illustrates the components used within the reaction cavity of the apparatus. The top row, from left to right, shows the bottom half of a pyrophyllite cylinder which is used for pressure transmission, as well as electrical and thermal insulation. An electrical resistance pressure calibration circuit is shown next, followed by the remaining half of the pyrophyllite cell. Directly below these items lie a metal electrical contact disk, a cylindrical plug of metal reactant, a graphite plug, an additional metal

reactant plug and contact disk. A sectioned assembled unit is directly to the right, followed by a nylon sleeve which provides electrical insulation for the portions of the high pressure pistons extending into the high pressure cylinder bore. The above configuration has been found suitable for reaction studies because of its simplicity, and because reaction surfaces are broad and essentially isothermal. Where reaction between the reactants under study and pyrophyllite occurs, either a chemically inert protective sleeve or the arrangement shown in the bottom series of the

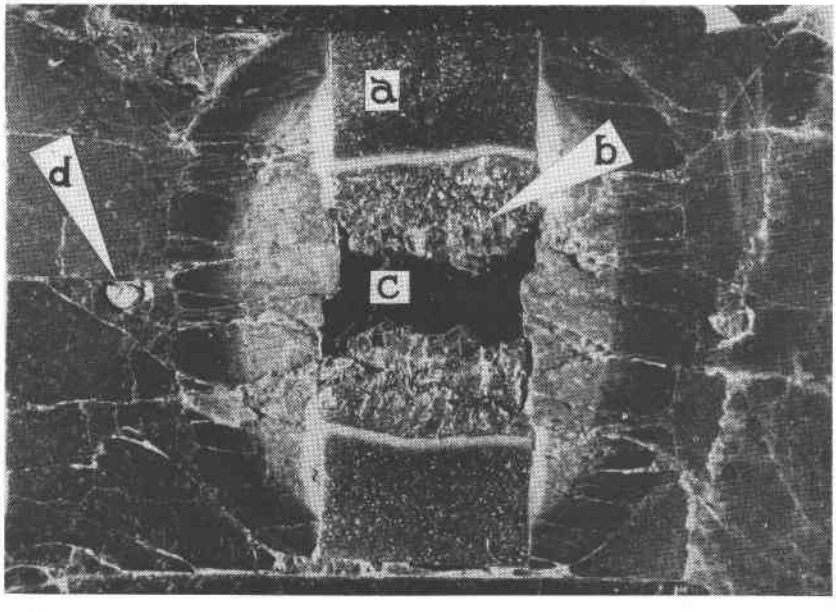

FIG. 4. A cross-sectioned specimen recovered from a supported stepped piston-cylinder apparatus after being subjected to high pressure and high temperature. Synthetic diamond can be observed at the metal-graphite interface. Width of the section is 12.5 mm.

Figure is used. The graphite—pyrophyllite interface is non-reactive. Contamination by diffusion through the graphite, however, must be considered. Since the basic geometry illustrated both for reactants and passive constituents is universally applicable to all present types of static pressure equipment, and is suitable for diamond growth, other more sophisticated techniques developed for special effects will not be described.

Figure 4 shows a cross sectioned complete specimen recovered from the pressure vessel. The constituents from center top to bottom are: (a) un-

reacted iron; (b) iron carbides[1] and diamond; (c) unreacted graphite. The thermal environment is illustrated by the light gray elliptical zone surrounding the reactants. Here pyrophyllite has been altered to coesite and kyanite (Giardini *et al.*, 1961). The pressure measuring circuit is shown at (d).

Figure 5 provides a view of a core recovered from an arrangement illustrated by the bottom row of Fig. 3. The reactants consisted of an iron rod placed within a graphite tube. The latter were both placed within a thin walled iron sleeve. Area (a) shows diamond crystals covered with unreacted graphite. Intermixed and behind the diamond are iron carbides.[1] Zone (b) constitutes a central core of iron silicate.[2] The latter formed as a result of silica diffusion from the outer pyrophyllite cylinder, and provides a graphic example of the surprising mobility generally encountered in solid state reactions carried out at high pressures and temperatures.

Analytical work has been performed by the following techniques: (a) optical microscopy, (b) electron microscopy, (c) emission spectroscopy, and (d) *x*-ray diffraction and fluorescence.[3]

These studies have shown that the mechanism of diamond synthesis under conditions of static high pressure and high temperature involving multi-component systems, is one of solution of carbon in a suitable solvent to a state of supersaturation. The thermodynamic instability of the resultant solution requires decomposition, and yields subsequent crystallization of the precipitated free carbon. Whether the latter crystallizes as diamond or graphite appears primarily dependent upon the local pressure-temperature environment. Theoretical data on the diamond-graphite equilibria derived by Berman and Simon (1955) have been experimentally verified within specified limits of probable error (Figs. 9 and 10). The minimum temperature for diamond growth at a given pressure in any usable system is defined by its carbon saturation limit. Some minimum values of pressure and temperature are given in Table 1.

The behavior of the metal carbon solvents listed above falls into two general categories: those prone to form stoichiometric carbon compounds (carbides), and those which are not. Examples of the former are Fe, Mn, Cr, and Ta. Pt, Ni and Co exemplify solvents not prone to form carbides.

[1] It may be of interest to mention here that the highest carbon iron carbide observed prior to diamond formation corresponds to a chemical formula of FeC. The material possesses a higher physical hardness and chemical stability than the common carbide of iron, Fe_3C.

[2] Characterization is not yet complete. The weight ratio of Fe:Si is approximately 1:1. Additional data will be published later. In general, it resembles muscovite.

[3] See accompanying article by J. A. Kohn and D. W. Eckart.

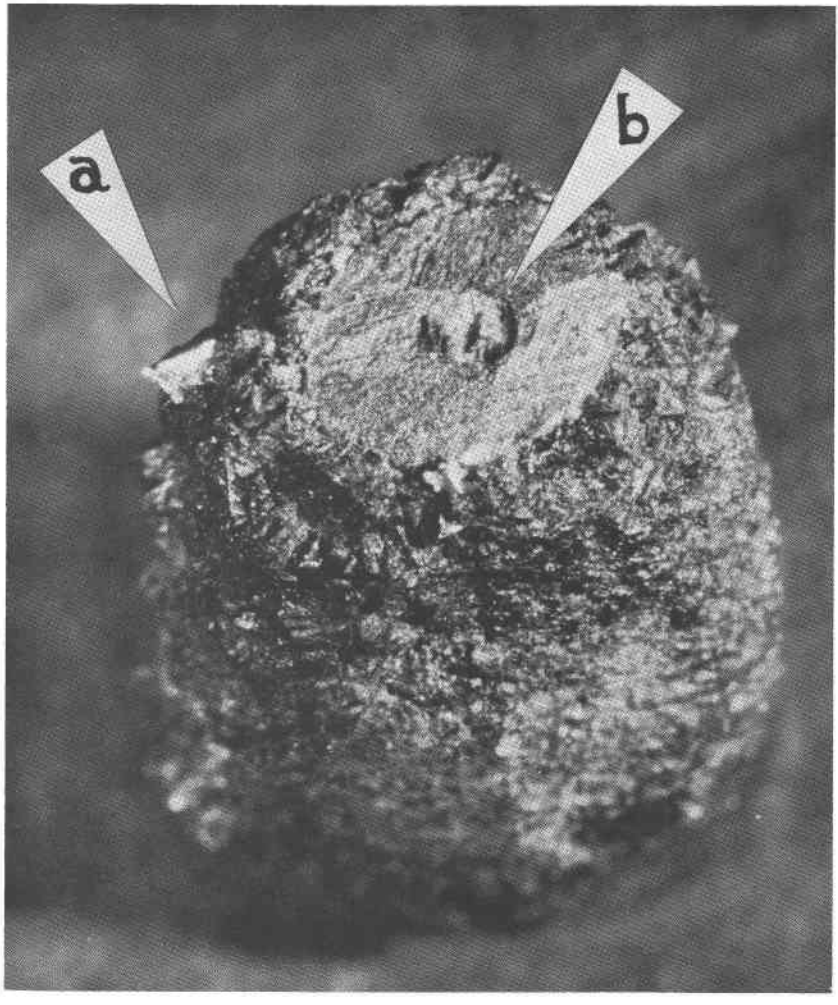

FIG. 5. An example of diamond growth from an iron-carbon system. Note the octahedron protruding from the top left. The crystal edge showing is approximately 2.7 mm long.

Since carbides of nickel and cobalt can be formed, perhaps some clarification is in order.

The reactions generally required for their formation are of a metal-gas type carried out at relatively low pressures and temperatures for extended periods (Hofer and Peebles, 1947, and Hansen, 1958). The respective carbides reported (Ni_3C, Co_3C and Co_2C) are of powder form, of poor crystallinity and reactive. They frequently find use as catalytic

reagents. They are classed as metastable (Hansen, 1958). The carbide of nickel, Ni_3C, also has been formed by solution of carbon in nickel. Temperatures over 2000° C. at normal pressure are required, followed by rapid thermal quench to below 1000° C.

Thus far, neither a recoverable nickel carbide nor microstructural evidence of the existence of such a compound has been observed in the diamond making range of pressure and temperature. Evidence has been noted, however, of a free nickel carbide in high pressure reactions carried to temperatures far in excess of the limit for diamond growth, followed by rapid thermal quench. The latter occurrence corresponds to the carbon solution in nickel at high temperature and normal pressure described above. The carbide is similarly considered unstable.

Residual microstructures observed from successful diamond experiments with the cobalt-carbon system indicate the probable occurrence of a series of cobalt carbides at high pressures. The latter is in accord with the fact that cobalt carbide(s) formed at normal pressure are considered slightly more stable than those of nickel (Hansen, 1958). Figure 6 shows three different structural patterns most frequently observed. *X*-ray diffraction studies, however, have determined the presence of only elemental cobalt and graphite. Such carbides of cobalt that the microstructures might indicate, therefore, are normally unstable. Decomposition is complete. Note the sharp segregation of constituents. No evidence of a platinum carbide has been observed in work on the platinum-carbon system.

On the basis of diagnostic evidence from residual products, the mechanism of diamond synthesis in the case of non-carbide forming solvents such as nickel or platinum, or alloys thereof, apparently is that of simple binary (or ternary, etc.) solution carried to supersaturation. That the latter prevails is evidenced by the fact that diamond growth is spontaneous.

An idea of the degree of carbon solubility in nickel is given in Figure 7. The latter, 7(a), shows a cross section of a nickel plug heated to a "normal" diamond growth temperature (1475° C.) but maintained at a slightly deficient pressure (45–50 kilobars) for a period of 2 minutes. The white area is nickel and the gray is dissolved carbon. The content of dissolved carbon in the reaction zone is approximately 36% by weight. On an atomic weight per cent basis, the latter would provide an approximate NiC_3 compositional formula. A similar degree of solubility has been observed for iron.

That the carbon was truly in solution is illustrated by Fig. 7(b) and 7(c). Again the white areas are nickel and the gray to black recrystallized graphite (photographed in crossed polarized light). The coarse and

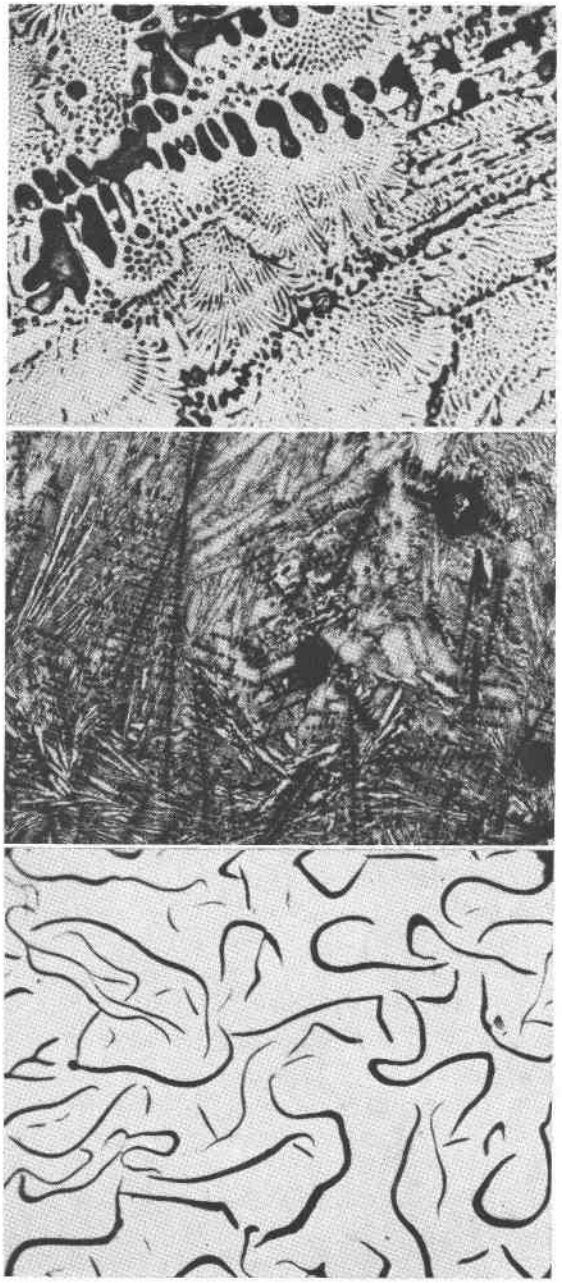

FIG. 6. Three examples of microstructures observed in a high pressure and high temperature cobalt-carbon reaction.

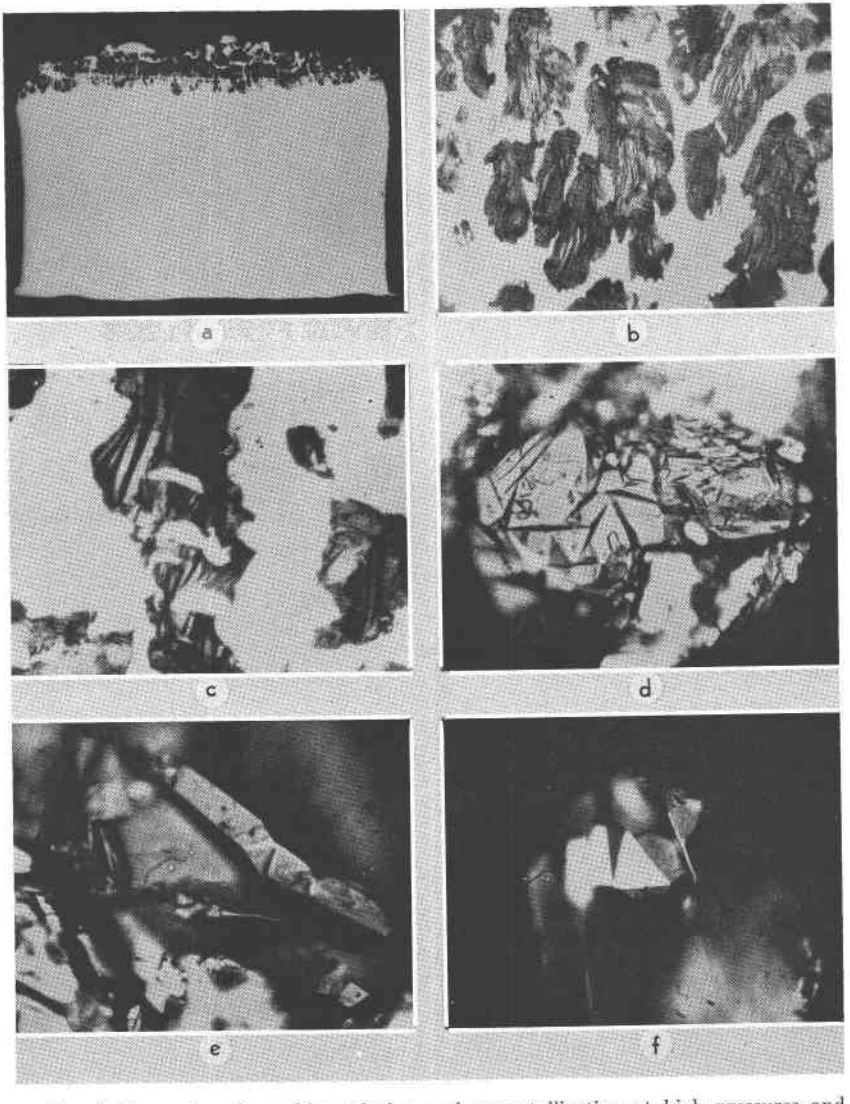

FIG. 7. Examples of graphite solution and recrystallization at high pressures and temperatures in simple metallic solvents. (a) Cross sectioned nickel plug. Width = 5 mm. Carbon solution is at top. (b) Microstructure of a nickel-carbon solution (X polarized light, 500×). (c) A magnified view of an area in (b). (1000×). (d) Recrystallized graphite from a platinum-carbon solution. (e) Essentially single crystal recrystallized graphite from a Pt-C solution (1500×). (f) Additional recrystallized graphite from a Pt-C reaction (1500×).

TABLE 1. OBSERVED MINIMUM PRESSURES AND TEMPERATURES OF DIAMOND FORMATION FOR SOME METAL-CARBON SYSTEMS

System	Pressure[1] (kilobars)	Temperature[2] (° C.)	Hold Time (Minutes)
"Inconel"+Graphite	45	1150°	2
Mn, Cu (12/1 wt. ratio)+Graphite	48	1400°	2
Cobalt+Graphite	50	1450°	2
Mn, Co (12/1 wt. ratio)+Graphite	50	1450°	2
Mn, Ni (12/1 wt. ratio)+Graphite	53	1475°	2
Nickel+Graphite	55	1460°	2
Pt, Co (4/1 wt. ratio)+Graphite	55	1500°	2
Iron+Graphite	57	1475°	2
Manganese+Graphite	57	1500°	2
Tantalum+Graphite[3]	65	1800°	2
Platinum+Graphite[3]	70	2000°	2
Chromium+Graphite[3]	70	2100°	2

[1] The stated pressures are those measured at room temperature prior to elevation of temperature. Measurements are based on the electrical resistance values of the pressure-induced transitions of 0.5 mm diameter bismuth and barium wires encased in 3 mm diameter AgCl. Reference values of 25.4, 26.9, 60 and 90 kilobars have been used. Margin of error is believed to be approximately 1% at 30 kilobars, 3% at 50 and 5% at 70 kilobars.

[2] Temperatures at the location of diamond formation are believed to be correct to within 5% at 1500° C. and within 10% in the vicinity of 2000° C. Thermocouples of Pt-Pt (13% Rh) have been used.

[3] The geometry of reactants used in these experiments was that of an elongated metal rod enveloped by a graphite sleeve. Some nickel contamination was experienced due to diffusion from the electrical contact disk (Fig. 3). The remaining experiments consisted of a vertical stacking of metal graphite-metal solid right circular cylinders.

regular microstructure is fully different from both the residual bulk unreacted graphite and that in contact with but undissolved in the metal. Figure 7(c) is an enlarged portion of 7(b). Figures 7(d), 7(e) and 7(f) show specimens of essentially three dimensional single crystal recrystallized graphite observed in pure platinum. The latter was reacted with graphite at approximately 2000° C. at 80 kilobars. No diamond was formed. *X*-ray diffraction of reaction products showed only graphite and elemental platinum. Diamond has been readily synthesized with platinum containing small amounts of nickel or cobalt. The latter tend to reduce temperature, and therefore, pressure requirements.

The reaction mechanism in carbide forming solvents constitutes a sequential formation of carbon compounds with increasing stoichiometric carbon content.[1] The sequence proceeds, in the presence of excess carbon, to the formation of an "ultimate carbide" having the highest possible

[1] Determined by analysis of residual products.

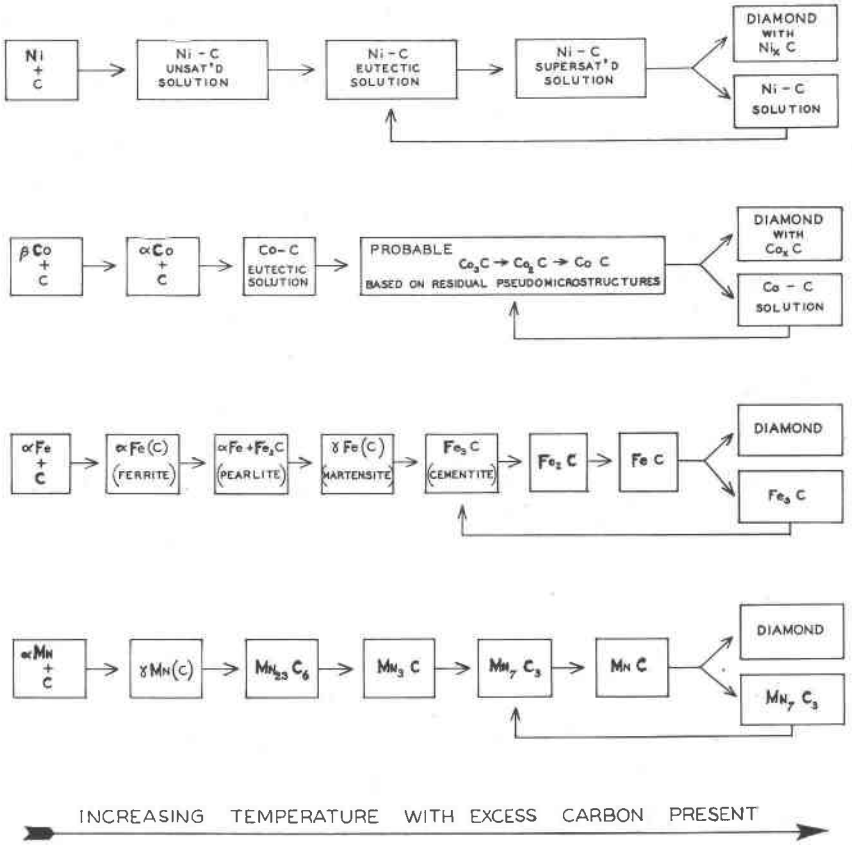

FIG. 8. A flow diagram illustrating the sequential nature of metal-carbon interaction (in an excess of carbon) under high pressure as a function of temperature. The designated presence of Fe_2C is tentative.

stoichiometry of carbon. The latter, again in the presence of excess carbon, decomposes to the next lower carbide with the liberation of free carbon atoms. The chemistry is regenerative by reaction of the "lower carbide" decomposition product with additional unreacted graphite. The sequence has been observed both for pure iron[1] and manganese,[1] as well as chromium and tantalum both containing small amounts of nickel. Nickel was added to the latter two so as to reduce PT requirements to a more readily manageable range.

In view of the mechanism described above, the reaction philosophy of

[1] The "ultimate carbides" observed in the iron-carbon and manganese-carbon systems for the P-T values covered correspond to FeC and MnC, respectively.

Slawson's earlier work on carbon recrystallization appears to have been sound (Slawson, 1953). Had the decomposition of the mercury-carbon system, HgC_2, been susceptible to greater experimental control, synthetic diamond might well have resulted.

Typical examples of each class of solvent is given in Fig. 8. The flow diagrams illustrate the case of a simple binary solution (Ni-C), as well as that for a quasi-simple solution (the probable unstable carbides of cobalt, Co_3C, Co_2C, and possibly CoC). Manganese and iron are representative of solvents yielding residually stable carbides.

Pressure-temperature diagrams are given in Figs. 9 and 10 for the nickel-carbon system and the manganese-carbon system, respectively. Both include the Berman and Simon data for the carbon-carbon system. Estimated limits of error are included. Slightly different values have been reported recently by Bundy, *et al.* (1961) for the nickel-carbon system. The difference may be explained on the basis of variation in measurement due to the differential elastic and thermal characteristics of complex reaction cell design. Different materials transmit pressure and heat with

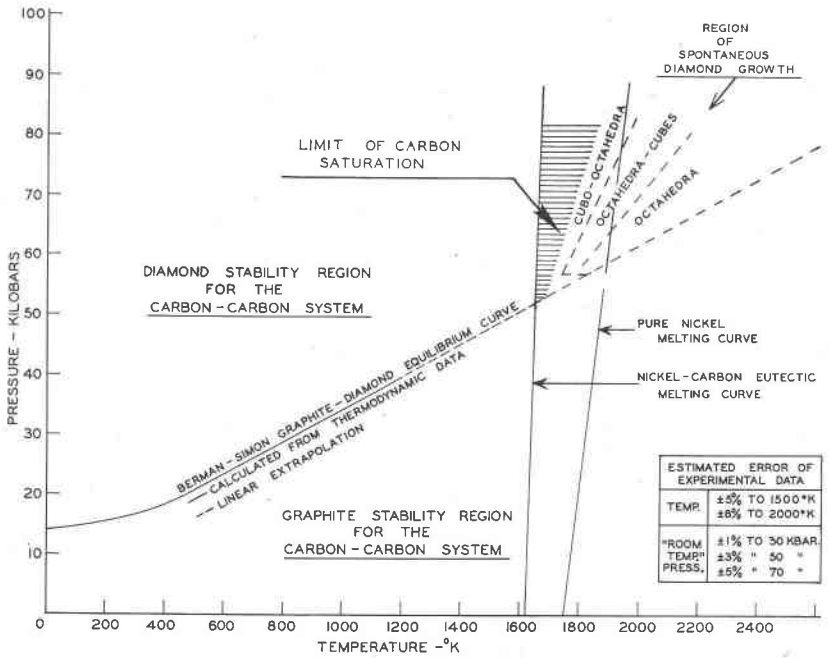

FIG. 9. Composite pressure-temperature diagram for the systems carbon-carbon and nickel-carbon. Pressure values are referred to the bismuth transitions taken at 25.4, 26.9 and 90 kilobars and that for barium at 60 kilobars. Temperature values were determined by thermocouple measurement.

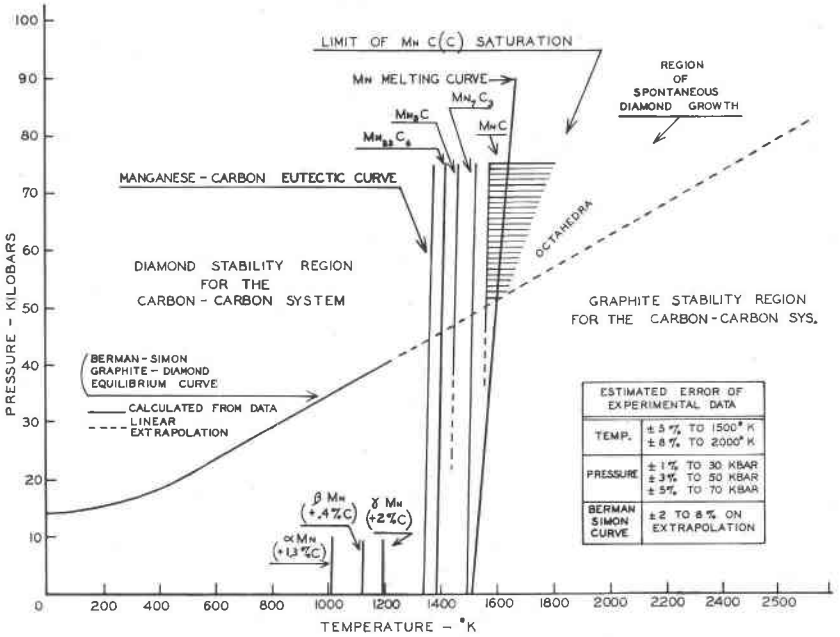

FIG. 10. Composite pressure-temperature diagram for the systems carbon-carbon and manganese-carbon. Pressure values are referred to the bismuth transitions taken at 25.4, 26.9 and 90 kilobars and that for barium at 60 kilobars. Temperature values were determined by thermocouple measurement.

different efficiencies. An accurate ability to concurrently measure high pressures and temperatures remains to be developed.

During the course of work on diamond, it has been observed that crystals synthesized from both nickel and cobalt invariably contained an internal contamination of the metal solvent. The degree of contamination (and crystal morphology) was found to be dependent upon the temperature during crystallization. The presence of impurity generally could be readily detected by a visual discoloration in shades of yellow, green or brown. A more quantitative determination can be made either by determining the degree of magnetism, by analytical optical techniques, or x-ray diffraction. Diamond grown from Fe or Mn solutions, on the other hand, could be made colorless and chemically pure.

The fundamental cause for this difference in purity has been gleaned from a study of analytical data obtained from the spectrographic and x-ray diffraction study of the diamond and related products from the various chemical systems. Contamination is directly related to the degree of structural compatibility of phases present during crystallization with

that of diamond. Nickel and cobalt containing limited amounts of carbon both possess structures which almost perfectly match that of diamond. These phases, consequently, are easily accommodated within diamond as dispersed but systematically oriented inclusions (Lonsdale *et al.*, 1959, and Kohn and Eckart, in this issue of *Am. Mineral*). The carbide forming systems studied thus far have not been found to possess structurally compatible coexisting phases.

The concentration of epitaxially included matter has been observed to be roughly inversely proportional to the temperature at crystallization. In addition, the concentration appears to influence both the pattern of growth as well as the resultant habit. The following sequential correlation has been observed:

a) At minimum pressures and temperatures, cube morphology invariably prevails. The impurity level is so high they are rendered completely opaque to visible radiation and they are structurally weak. Not only is the content of epitaxial inclusion high, but random inclusion of other coexisting phases also is marked. The latter frequently appears to function as nucleation surfaces around which diamond crystallization commences. This type of diamond is so impure that it is questionable as to whether such specimens can properly be considered chemically as diamond. Crystal growth is observed to proceed either as a random propagation of lamellae parallel to and upon (100), or as spirals terraced parallel to the cube edges. The occurrence of spirals has been reported earlier by Bovenkerk (1961), and Tolansky and Sunagawa (1959 and 1960).

b) At higher pressures and temperatures, a diminished content of "structural" impurity is observed. Crystals may transmit somewhat in the visible region, and the development of octahedral faces become apparent at the corners of the cube. Growth appears to continue parallel to (100), but lamellae now are systematic; the direction of propagation being approximately normal to the cube edges.

c) At higher levels of pressure and temperature, diamond of corresponding higher chemical purity are realized. Relatively transparent cube-octahedral, and sometimes cube-octahedral-dodecahedral, forms are found. The trace of growth layers on (100) are observed to run parallel to the edges of octahedral planes. The latter is considered indicative of normal (111) diamond growth free of influence from the chemical environment which was observed at lower pressures and temperatures.

d) At relatively high pressures and temperatures within the diamond forming region, the octahedral habit predominates (Fig. 9), and the clarity and purity of the crystals are accordingly greater. Growth is observed to propagate upon and parallel to (111), in directions normal to (111) edges. The observations described above are illustrated by the correspondingly designated sections of Fig. 11.

Although the content of epitaxially included matter is approximately inversely proportional to the temperature at crystallization, both its chemical composition and crystal structure remain relatively stable. The formula for that of nickel has been suggested as Ni_xC, with x greater than four (Lonsdale *et al.*, 1959). A similar formula is applicable to the "structural inclusion" observed with the cobalt-carbon system. In view of the fact that the proposed mechanism of direct chemical solution of carbon

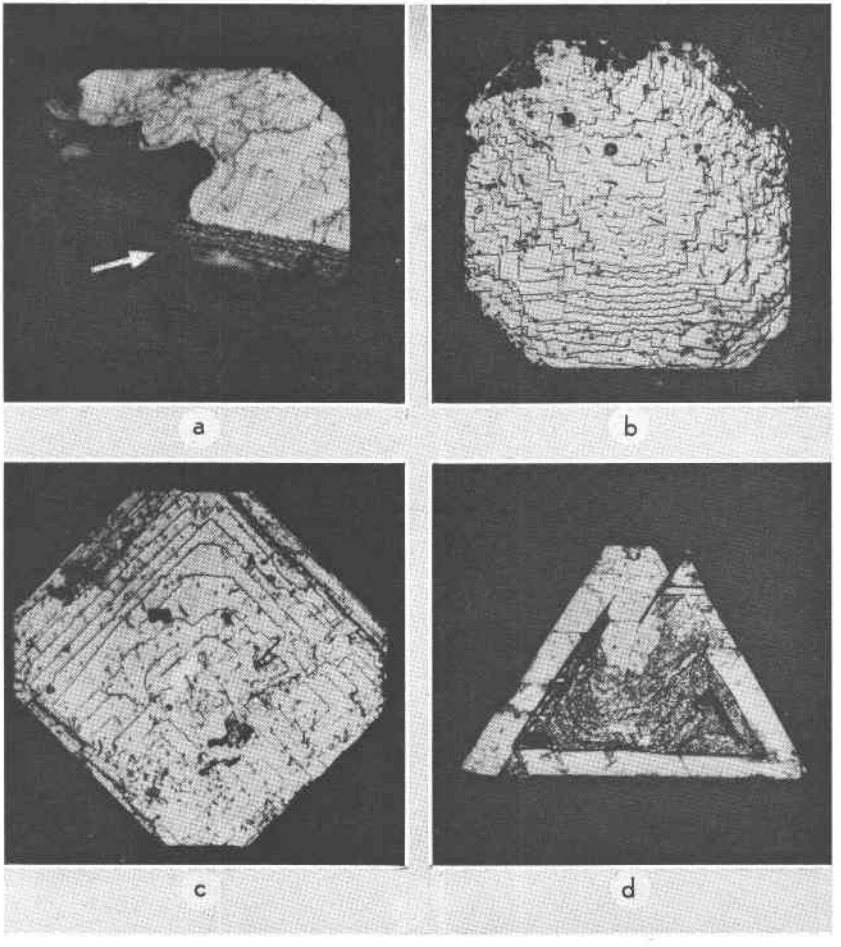

FIG. 11. (a) an example of surface texture commonly observed on highly impure, opaque, but well formed diamond cubes. The exposed lower right section of the crystal (see arrow) illustrates the occurrence of lamellar growth parallel to (100). (b) a somewhat less impure cube with noticeable (111) development at the corners shows an example of growth on (100) with the direction of propagation approximately parallel to [100]. (c) the cube face of a relatively pure cube-octahedron exhibiting growth propagation on (100) in directions essentially normal to the edges of (111). (d) the surface of a diamond octahedron illustrating growth on and parallel to (111) with directions of propagation normal to the edges of the face.

followed by precipitation and recrystallization is based upon the study of residual reaction products, the possibility that phases present during diamond crystallization may provide a catalytic interaction cannot be categorically ruled out. The observed range of structural compatibility of

coexisting phases from excellent to non-existent, as well as the sequential nature of reactions preceding diamond formation from simple solution to stable carbide formation, and, with respect to the latter, the formation of carbides of limited stability to those stable under the widest range of environment, suggests that the probability of a catalytic mechanism is questionable.

The strongest motive for the concept of catalysis probably has been the presence of the Ni_xC phase in synthetic diamond, since the most commonly used chemistry generally includes nickel. The great excess of dissolved carbon existing in a saturated solution prior to decomposition and diamond growth (Fig. 7 (a)) in comparison to residually included matter such as Ni_xC implies, however, that the latter simply represents an entrapped incidental nickel-carbon composition from the depleted solution which circumstantially has a crystal structure similar to that of diamond. The inclusion need not exercise an essential influence on diamond formation. The probability exists, in fact, that diamond may be influential in the crystallization of the Ni_xC (or Co_xC) since it has only been observed as an epitaxially included phase. That the latter does exert an influence upon diamond morphology has been mentioned earlier. The effect, however, appears to be an adverse one.

At higher temperatures of crystallization, it is observed that both the total yield of diamond and number of individual crystals generally is greater, whereas size and impurity content (non-carbide forming solvents) is lower. By analogy, these characteristics are similar to ordinary crystallization processes from chemical solution. The above can be interpreted as representing a rapid supersaturation as functions of temperature and reactant concentration resulting in widespread precipitation, nucleation and growth. The existence of lower concentrations of included matter can be taken to indicate simply a more complete local depletion of dissolved carbon independent of influence on diamond crystallization. Material transport is observed to be remarkably vigorous under conditions of high pressure and high temperature (Figs. 6 and 7(a)).

Several experiments have been conducted to test the concept of crystallization from solution. Reactions designed to precipitate the metal solvent from solution so as to induce a premature, controlled state of carbon supersaturation have been carried out. Success was achieved through precipitation of the metal as insoluble silicates, primarily as garnet-type compounds of cobalt, iron and manganese, respectively. Diamond in the form of colorless octahedra[1] could be crystallized in the region of secondary precipitant reactions, whereas in an adjacent area of the same experi-

[1] Due to the intimate and rapid initial crystallization, the various garnet precipitants commonly are observed both as intergrowths, overgrowths and inclusions within the diamond.

ment free from secondary precipitation, cube crystals of high impurity content were obtained. The results support the mechanism proposed.

Since the temperature of supersaturation and spontaneous crystallization can thus be controlled, by inference, pressure requirements also are subject to manipulation. The two, however, still must meet fundamental thermodynamic requirements for diamond stability.

Further experimentation performed to study the mode of diamond formation concerned studies on carbon solution, precipitation and recrystallization from non-metallic solvents. Several ammonium compounds were chosen. Examples have been given earlier. Successful solution and spontaneous precipitation have been successfully achieved. At pressures normally required for diamond growth, however, exceptionally high temperatures have been found necessary to achieve supersaturation (approximately 2000° C. and above). Pressure requirements for diamond at these temperatures are severe. Only single crystals of recrystallized graphite were obtained. These were, however, of excellent crystallinity and chemical purity.

An additional experiment was chosen to test the solution concept. In this case, a carbide former and non-carbide former constituted the metal solvents for carbon, with the idea being that the selected carbide former would form a stable compound at a lower temperature than carbon supersaturation could be achieved in either of the two metals. An added criterion was that the temperature of supersaturation of the carbide former be higher than that of the non-carbide former at any given pressure in the achievable diamond growth range. Nickel and chromium were chosen as qualifying solvents. A thermal gradient was imposed on the graphite-metal system with the higher temperature being in the graphite environment. The test was to determine whether the carbide former would precipitate dissolved carbon from the solution in the cooler portion of the metallic solvent; the result anticipated being a premature supersaturation of the non-carbide forming solvent (nickel) in the hotter zone at the graphite interface. The latter might be expected to occur as the result of the imposed concentration gradient on the dissolved carbon, thus inducing an accelerated diffusion rate (pressure and temperature held constant). The experiment succeeded and the objectives were confirmed. Figure 12 shows a cross sectional view of a recovered specimen. The needle-like phase in the central portion of the metallic zone is Cr_3C_2. It was observed that diamond could be crystallized at pressures and temperatures somewhat lower than normally encountered for nickel. Since the above situation is quite analogous to those which exist for commercial alloys such as inconel and nichrome, the explanation may also apply to them.

Solution mobility and lower carbon saturation temperatures for

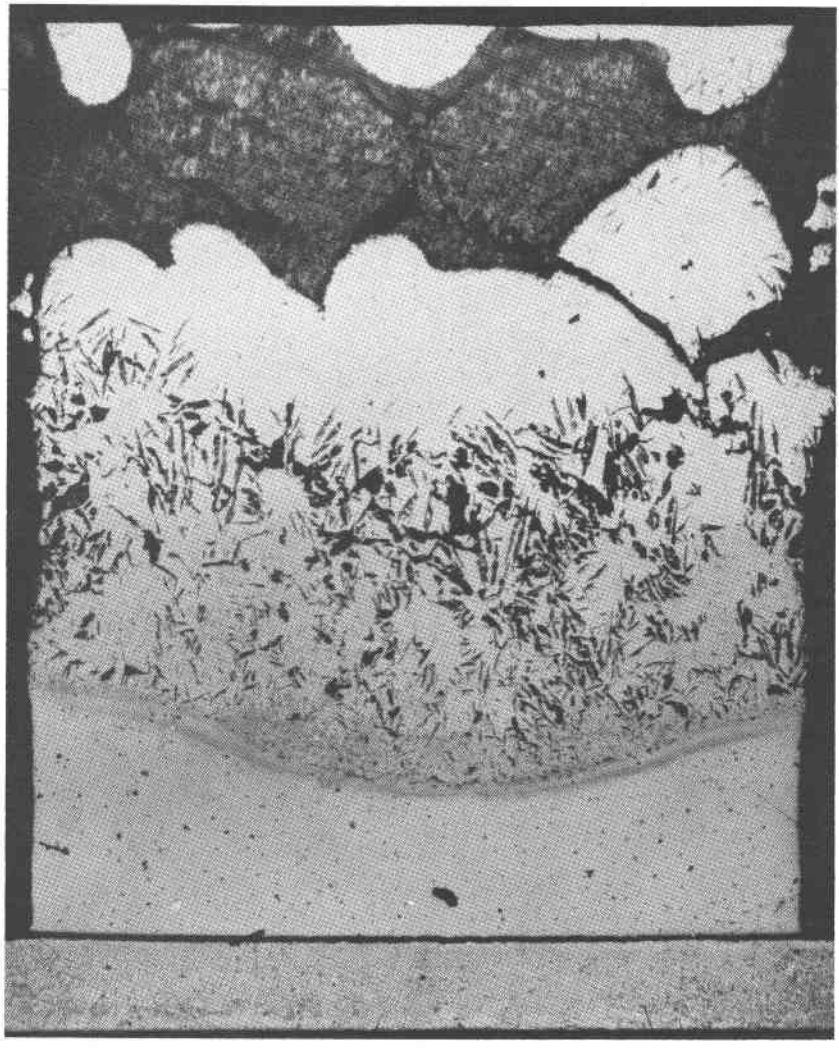

FIG. 12. A cross sectioned specimen showing a nickel-chromium-carbon reaction carried out at high pressure and temperature. The needle-like phase in the metallic area is Cr_3C_2. The mottled gray-black area at top center is unreacted graphite.

metallic solvents also may be achieved by the use of lower melting neutral elements such as copper; for example, systems such as Mn-Cu-C, or Ni-Cu-C.

An experiment performed utilizing a somewhat similar combination of solvents, namely a carbide former and non-carbide former, but directed to

a different objective, involved the reaction of a manganese-nickel mixture of approximately 12:1 ratio by weight, respectively, with carbon. The plan of the test was to maintain the temperature at the relatively high value necessary for diamond formation through reaction of manganese and carbon (approximately 1500° C. Fig. 10), whereupon the manganese would be progressively removed from the solvent alloy by carbide formation. The residual manganese-nickel composition was expected to be displaced towards the relatively low melting eutectic at a 3:2 weight per cent ratio (approximately 1000° C.). The effects looked for were both an improved solubility and transfer rate of carbon to the manganese reaction for prolific crystallization of high quality diamond. Since the temperature maintained was excessive for diamond formation from the low melting "reduced" Mn-Ni solvent, diamond growth was realized essentially from a simple Mn-C reaction. Crystals both of high purity and crystallinity have been obtained by use of this technique. The only included phase observed in a well performed experiment has been occasional recrystallized graphite, generally oriented along (111) planes. Figure 13 shows several diamond crystals representative of the better quality specimens obtained from (Mn, Ni)-C systems. Their size is approximately 0.3 mm.

Studies performed at constant pressure, with temperature and time variable, have provided additional support for the proposed growth mechanism. It has been observed generally that both the rate of growth and crystal size were subject to reasonable temperature control. For example, as previously mentioned, higher temperatures (within proper P-T bounds) usually yield a greater number of crystals but of smaller size. The situation is reversed at lower temperatures, primarily due to a lesser number of nucleation sites. In addition, crystallization, normally initially prolific, is observed to diminish rapidly. The total yield from a three minute experiment is not remarkably different from a nine minute one. New crystal formation is not rapid under steady state conditions. Following initial precipitation and crystallization, a system rapidly achieves equilibrium. Although new diamond formation essentially terminates, growth in crystal size is observed to occur through coalescence of existing crystals. The more fluid a chemical system and the longer the time, the more perfect is the coalescence. Coalescent growth also is a commonly observed phenomenon with the highly covalent material, SiC.

By lowering the temperature, precipitation can be reinitiated. By raising the temperature, supersaturation can be re-established with subsequent spontaneous precipitation. By cycling, within proper pressure-temperature limits for a given system, new growth can be rhythmically

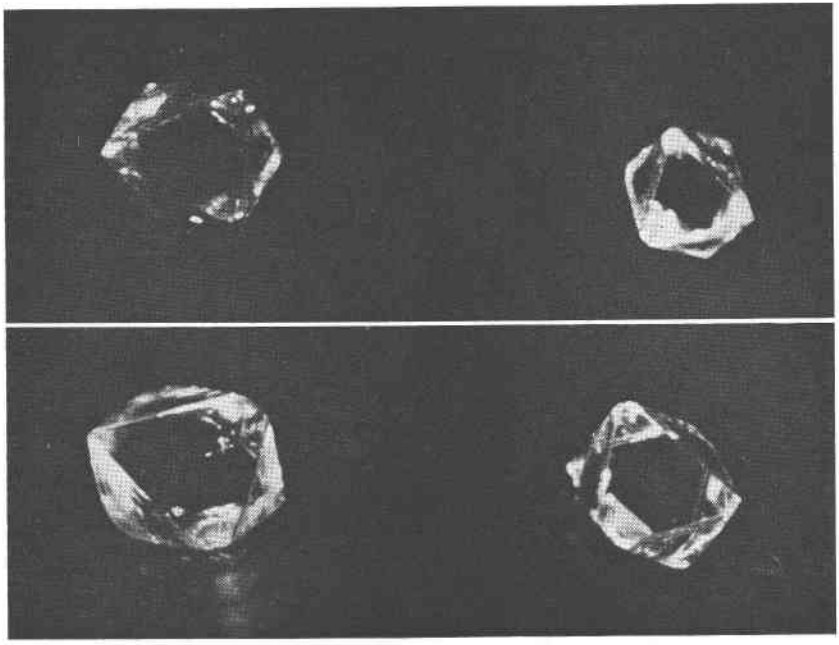

FIG. 13. Crystals of synthetic diamond. Approximate size is 0.3 mm.

maintained reasonably well. Rapid fluctuation, especially where the temperature falls below the growth boundary, yields markedly lamellar specimens, generally with environmental inclusions between octahedral lamellae. Relatively large crystals may be obtained by either rapid and severe, or slow and moderate variation. The first provides rapid growth but crystals of poor quality. The latter requires additional time but yields better quality specimens typical of growth under quasi-equilibrium conditions. Crystals approximately 3 mm in size have been grown in a matter of minutes in confirmatory experiments (Fig. 6).

Figure 14 shows several examples of growth by coalescence. Note both the compatible orientation on (111) of coalescing constituents and the 60 degree rotational freedom permissible on the octahedral plane.

The orientation of coalescing units appears to reflect that of the decomposing phase (or phases). The latter provides units of nascent carbon which are patterned after its own structure. Subsequent recrystallization yields diamond. Most successful reactions experienced thus far essentially occur in the solid state. The dendritic texture of incipient coalescence is illustrated by Fig. 14(c) and (d). The coalescence of larger, more mature units is shown by Fig. 14(a) and (b).

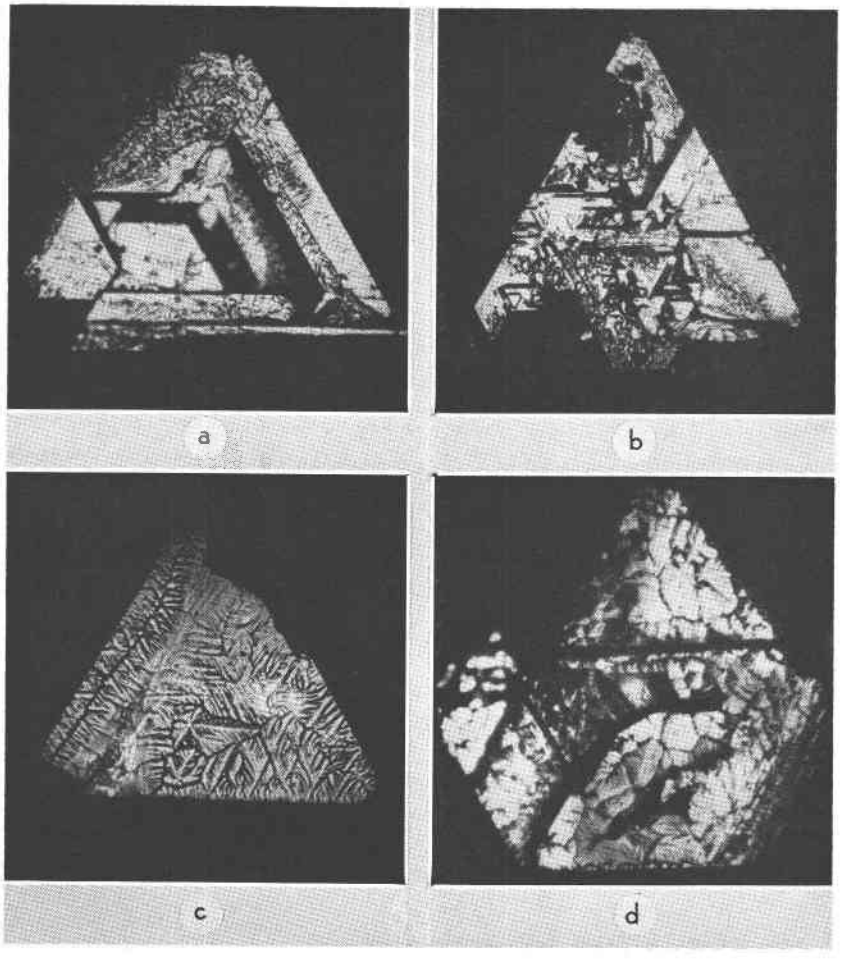

FIG. 14. Examples of crystal growth through coalescence. Sections (a) and (b) illustrate coalescence of relatively well developed units. Note both the parallelism of surfaces and the 60 degree rotational freedom of octahedral constituents. Section (c) provides an example of incipient coalescence and clearly shows the depositional pattern of nascent carbon from the decomposing solution. This particular specimen is typical of carbide forming systems. Noncarbide forming systems such as Ni+C display less linear dendritic textures which descriptively resemble the appearance of tobacco leaves. Section (d) not only provides an additional illustration of growth through accretion of carbon units, but also the formation of a macroscopic spinel-type twin. The predominating influences on twin formation appear to be the orientation and depositional rate of the decomposing phase(s) (see also the lower center of section (c)). The average size of the octahedral faces illustrated is approximately 0.3 mm.

A potential site for the formation of a spinel-type twin is shown in the lower central part of Fig. 14(c). Should additional growth predominate on the lower right sector of the "carbon dendrite" which displays a sixfold symmetry, an octahedral unit would develop having an orientation rotated 60 degrees with respect to the larger host unit. Figure 14(d) illustrates the development of a readily visible spinel-type twin. Propagation occurs through the accretion of the dendrite-like units of carbon as they precipitate from the solution. Both the orientation and the degree of development of coalescing units can explain either multiple internal or visibly recognizable twinning in diamond. The illustrations given in Fig. 14 support the statistical twinning mechanism proposed by Slawson (1950).

The veined or dendritic surfaces reported by Bovenkerk (1961) are explained in most cases by coalescent growth. Some textures do reflect, however, both physical and optical effects of included accicular phases such as Cr_3C_2, and $(Cr,Fe)_3C_2$. The latter are abundant in reactions such as inconel+carbon. Coalescence also conveniently provides a means for inclusion of both coprecipitated and non-coprecipitated phases which might be present in the system during diamond crystallization.

Low Pressure Epitaxial Diamond Growth

A recent method for achieving measurable diamond growth at low pressures and high temperatures has been described by Eversole (1962). Specific carbonaceous compounds such as saturated aliphatics having 1, 2 and 3 carbons, or carbon monoxide, are thermally decomposed in the presence of diamond. Temperatures of approximately 1000° C. are used concurrent with pressures ranging from partial vacuum for hydrocarbons to approximately 2000 bars for CO gas. The process is similar to those used for producing pyrolytic carbons (Walker, 1962).

Growth apparently can be described as epitaxial upon a diamond substrate. No diamond formation is reported upon any other substrate material. The degree of growth during any one experiment is very limited due to the accumulation of non-diamond carbon. Successful cyclic growth is reported, however, with proper periodic cleansing operations. Yields are given in terms of per cent increase in bulk weight of diamond powders.

The surprising feature of this type of reaction is the apparent serious violation of thermodynamic permissibility. At approximately 1000° C. and pressures ranging from partial vacuum to 2000 bars, not only is diamond itself of very low metastability, with a strong tendency for reversion to graphite, but any growth process also would be anticipated as highly unstable. The low limit of achievable growth for any given

experiment may reflect this probable basic instability. Since only specific carbon saturated carbonaceous materials were found to yield new growth, for example, ring structure hydrocarbons and other organics not containing methyl groups were unsuccessful, indications are that diamond bonding represents a fortuitous attraction between substrate surfaces and specific carbon decomposition products. Needless to say, the mechanism warrants further study.

Natural and Laboratory Genesis

In view of the nature of this report, perhaps some philosophical opinion is warranted with respect to an attempted correlation of laboratory research with natural diamond genesis. Prior to further consideration, however, the following limitations should be emphasized:

(a) diamond is known in nature only as a trace constituent in complex chemical systems whereas the converse is true of present laboratory experience; (b) the chemical systems examined in the laboratory are not similar to those associated with natural sources of diamond excepting for metallic meteorite occurrences; (c) to a very great extent, the factor of time is ignored.

On the basis of comparative evidence, the following observations may be worthy of attention: (a) thermodynamically derived pressure-temperature limitations for diamond stability apply also to primary diamond formation processes; (b) in localities having no history of severe shock, diamond growth occurred from solution; (c) diamond occurrences in regions having experienced severe shock and possessing chemistry incapable of carbon dissolution represent growth from direct transformation of graphite; (d) diamond in areas subjected to severe shock and possessing chemistry capable of dissolving carbon may have crystallized from solution and under appreciably less intense P-T conditions than required in situation (c); (e) an abundant bulk carbon content is not vital for diamond crystallization in multi-component chemical systems since "secondary" precipitation reactions can produce sufficiently high local concentrations; (f) crystalline inclusions of environmental minerals, for example, olivine and garnet (Mitchell and Giardini, 1953), may be associated either with crystallization induced by reactions of the type described by (e), or as a result of entrapment during coalescent recrystallization; (g) diamond of hexahedral morphology and high impurity content represent crystallization at lower limits of pressure and temperature for a given chemistry relative to the formation of clear octahedral crystals; (h) visible inclusions of oriented graphite crystals generally can be associated with crystallization either at upper limits of temperature or from a relatively fluid solution; (i) relatively abundant surface and internal graphite represents excessive temperature at any pressure as defined by the Ber-

man-Simon equilibrium curve for graphite and diamond; (j) trace impurities may result either from the inclusion of microscopic quantities of crystalline matter, or for selected elements such as aluminum and boron, as elemental substitutes introduced by post crystallization diffusion, and finally, (k) a lamellar microstructure represents a fluctuating environment of pressure or temperature (or both), with included matter between lamellae indicating severe fluctuation.

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