PREPARATION OF DIAMOND

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It would be good to be able to write a paper entitled "The Preparation of Diamond", in which all the factors affecting diamonds were nicely accounted for and the formation of diamond was completely explained. But the work which has been carried out on this problem indicates that diamond can form in several different ways, and that stubborn mysteries still surround some of them. This article, therefore, is more of the
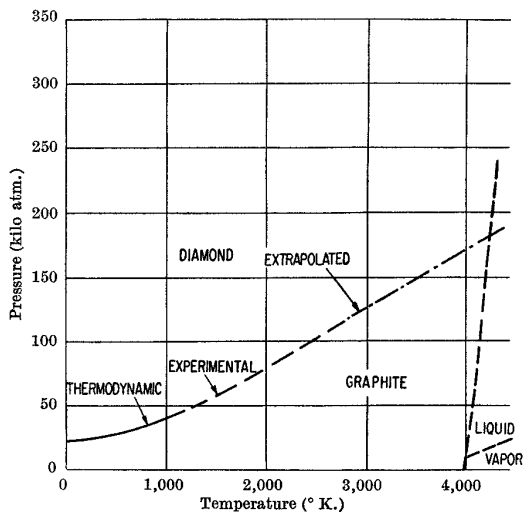

Fig. 1. Carbon phase diagram

nature of an interim report which describes the salient features of the knowledge obtained so far rather than a complete exposition of diamond formation.

All the observed cases of diamond preparation in our laboratory have occurred at pressures and temperatures appropriate for the thermodynamic stability of diamond. Fig. 1 shows a diamond-graphite equilibrium curve. For temperatures up to 1,200°K. the path of the curve has been estimated by Rossini and Jessup[i], Simon[ii] and others from thermodynamic data. For temperatures between 1,500 and 2,700°K., the path of the curve has been determined experimentally by observations of the growth or disappearance of small diamond crystals immersed in suitable media[iii].

The experiments which form the basis for most of this article were usually performed in a tapered piston apparatus capable of very high
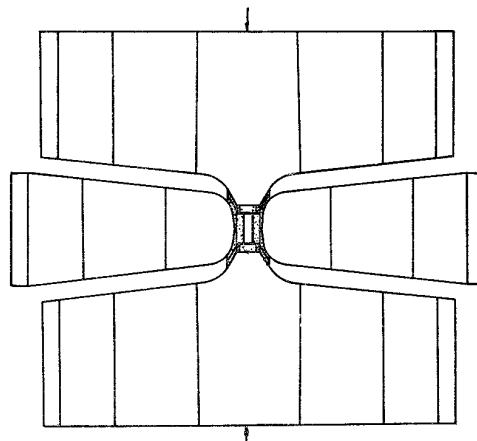

Fig. 2a. The 'belt', ultra-high-pressure, high-temperature assembly

pressures which enabled us to attain diamond stability at high temperature. Figs. 2a and 2b illustrate the tapered piston 'belt' apparatus which will be discussed in detail by H. Tracy Hall in a separate paper submitted for publication. Many
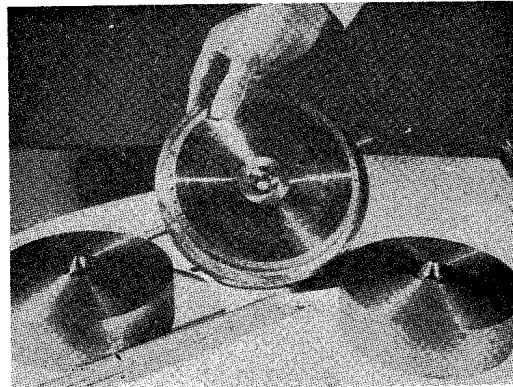

Fig. 2b. Photograph of apparatus

of the most promising systems were examined at several pressure-levels as appropriate apparatus was developed. Diamond does not always form where it is thermodynamically stable; this is what makes diamond synthesis so interesting.

The chemical systems which were studied in connexion with diamond synthesis can be conveniently grouped as follows: (1) direct transition, graphite to diamond; (2) systems involving carbon and oxygen; (3) systems involving carbon as salt-like carbides (4) miscellaneous chemical reductions; and (5) systems involving carbon dissolved in molten metals.

(1) Direct Transition, Graphite to Diamond

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The driving force for this reaction is the increase of density upon going from graphite to diamond. On the other hand, the high heat of vaporization of carbon (more than 100 k.cal./gm. mol.) implies that a high temperature will be necessary before much recrystallization of the
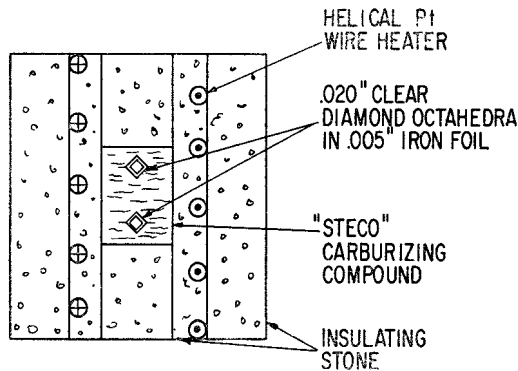

Fig. 2c. Diamond experiment

carbon occurs. Indeed, the usual range of temperatures for forming graphite industrially from petroleum coke, pitch, etc., is about 1,800-2,400°C., and some carbons graphitize only slightly at temperatures higher than these.

Some studies made in this laboratory of the graphitization of diamond at 0.1 and 20,000 atm. showed that the graphitization began at 1,500-2,000°C., depending on the particular diamond, and that, in general, higher temperatures were necessary to graphitize diamond at 20,000 atm. than at 0.1 atm. From the change in rate constant with pressure, the volume of the 'activated state' was estimated at about 160 c.c./mol., and the rate of graphitization, in atoms per second, was observed to be 10^5 times the rate of evaporation for, the same temperature. This indicated that the diamonds became graphitized by groups of atoms rather than atom-by-atom. For the reverse reactions, graphite to diamond, it would be reasonable to expect a similar reaction mechanism, because the strong intra-sheet binding forces in graphite would tend to make each sheet behave as a unit (as happens in the formation of 'graphite sulphate' or potassium-graphite). Although the coherent sets of sheets of atoms ('crystallites') in graphite or various carbons contain perhaps only 10^4 or 10^5 atoms, the pressure-volume energy of such a crystallite is large compared to kT at only moderate pressures (20,000 atm.). It is known that in some carbons the crystallites are rearranged only reluctantly to form commercial graphite even, at 2,700°C. and 1 atm. Thus the effect of increasing pressure is to slow down greatly any recrystallization of solid carbon, and this slowing-down more than offsets the thermodynamic driving force toward diamond gained by increasing the pressure. Experiments in which graphite was heated at high pressure served to squeeze the microscopic voids from the material, so that its density became nearly the theoretical density of graphite, but no diamond was formed, even at 120,000 atm. Perhaps diamond could crystallize from molten carbon at a sufficiently high pressure; but supposing the melting temperature of carbon to be 4,000°C. at this high pressure, one would estimate by an extrapolation that the required pressure would be in the neighbourhood of 200,000 atm. (The increasing incompressibility of graphite with pressure indicates that the required pressure might be even higher than this.) Such an experiment has evidently not yet been performed.

(2) Systems involving Carbon and Oxygen

Such systems are attractive because they are chemically versatile and tend to favour aliphatic rather than aromatic carbon-carbon bonds. The oxide mineral inclusions in natural diamonds[iv] suggest that perhaps certain oxides could play a part in diamond formation, perhaps through a shift in the carbon monoxide--dioxide equilibrium. In spite of all these attractive features, only graphite or amorphous carbon ever appeared as products from these systems, with one possible exception. This exception was the reduction of lithium carbonate by lithium metal at high pressures. The carbonaceous residue gave a feeble Debye-Scherrer pattern for diamond and scratched glass in a way characteristic of diamond (tiny helical chips were ploughed out of the scratches). A few tiny triangular faces, 1-10µ on edge, could occasionally be seen but not identified. Further experiments did not produce more abundant or larger crystals.

Other systems which were examined included similar reductions of carbonates, oxalates or formates by metals; the decomposition of iron, molybdenum or chromium carbonyls either pure or in solution in stannic chloride or molten salts; the decomposition of sugars and ketones; the electrolysis of molten carbonates; or finally, the attempted solution and transport of elemental carbon in various molten oxides such as borates, silicates, phosphates, 'blue ground', etc.

(3) Systems involving Carbon as Salt-like Carbides

These systems are attractive because they are comparatively rich in carbon, contain carbon

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atoms as free ions which could easily be built into a diamond lattice after a simple reduction, and are chemically active at low temperatures. However, only the high- pressure decomposition of lithium carbide by the outward diffusion of the lithium ever yielded any potentially diamondiferous product. The material from this decomposition gave a weak Debye-Scherrer diamond pattern, corresponding to a diamond content of about 1 per cent, and also scratched glass to leave the characteristic helical chips.

Other more disappointing reactions included the decomposition $2MgC_2 \rightarrow Mg_2O_3 + C$, the cyanamide reaction $CaC_2 + N_2 \rightarrow CaCN_2 + C$, the electrolysis of calcium or lithium carbides, and the substitution reaction $SiC + Ge \rightarrow SiGe + C$.

(4) Miscellaneous Chemical Reactions

Carbon disulphide is thermodynamically unstable at ordinary pressures and temperatures. At pressures about 45,000 atm. and 400°C. it was found to change into the black solid described by Bridgman[v]. In combination with various metals used as catalysts or reducing agents, carbon disulphide changed into amorphous carbon at higher temperatures and pressures. Similar reductions of chloroform, carbon tetrachloride or cyanides formed amorphous carbon.

Hannay's method was tried, in which lithium, light hydrocarbons and nitrogen-containing substances were heated together at high pressure. Again only amorphous carbons
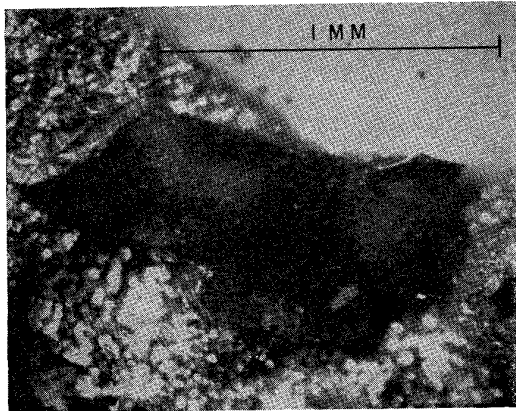
Fig. 3. Diamond in metallic matrix

appeared. The simple thermal decompositions of various hydrocarbons yielded similar products, and no diamond.

(5) Systems involving Carbon dissolved in Molten Metals

These systems turned out to be the most fruitful and also, unexpectedly, the most complex.

In our early work, when available pressures were still less than about 50,000 atm., some experiments were performed with molten aluminium, silver, and even iron. Of course, iron dissolved carbon in appreciable amounts; but the carbon which was precipitated from it was in the form of graphite. No matter how careful the change or how great the fluctuation of
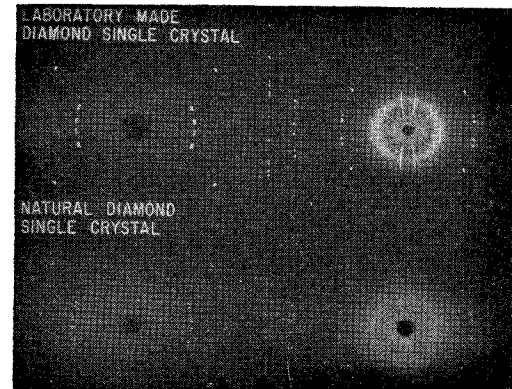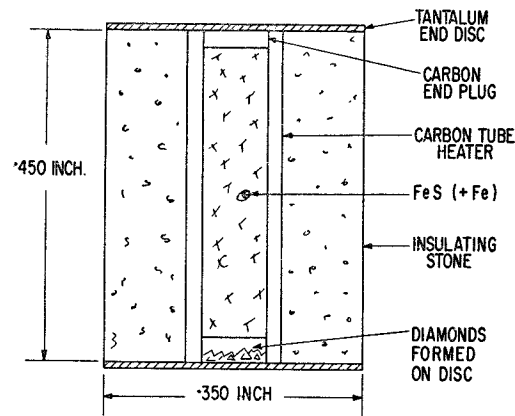
Fig. 4. Debye–Scherrer patterns

Fig. 5. Diamond experiment

temperature, when the pressure was less than 50,000 atm., only graphite resulted. In view of this, it is difficult to see how Moissan's claim to have formed diamond from molten iron-carbon mixtures inside his quenched iron could be sustained, since he could have reached at most only 10,000 atm[vi].

A number of experiments were performed using a metallic catalyst and carbonaceous material. One of the first experiments carried out involved heating some seed diamond crystals, iron and a carbonaceous steel-carburizing compound for 16 hr. at about 53,000 atm. and about 1,300°C. (Fig. 2c). Out of this there appeared two new diamond fragments with

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developed crystal faces, each of which was larger than any of the seed crystals. The identification was made by hardness tests and an X-ray diffraction pattern (Figs. 3 and 4). Attempted repetitions of this experiment did not produce diamond. However, it now appears that the iron-carbon system is quite complex at high
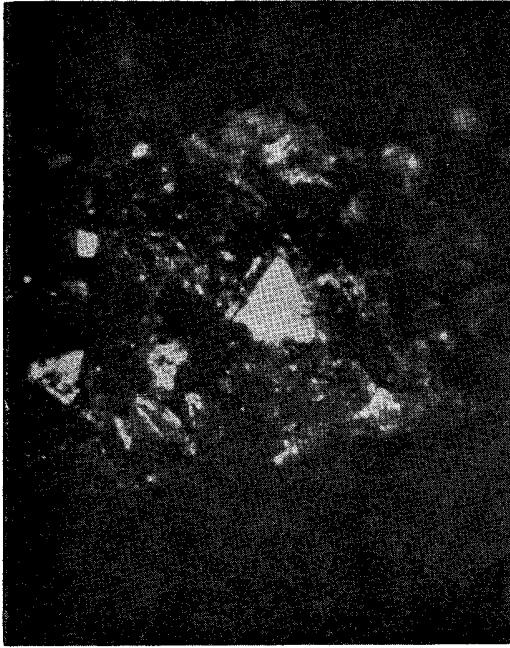

Fig. 6. Cluster of synthesized diamonds

pressures and temperatures. Several solid phases can form, among them FeC, Fe_3C, graphite and diamond; but which one happens to form depends upon slight variations in temperature, temperature change or chemical composition. Even at 100,000 atm., certain temperature
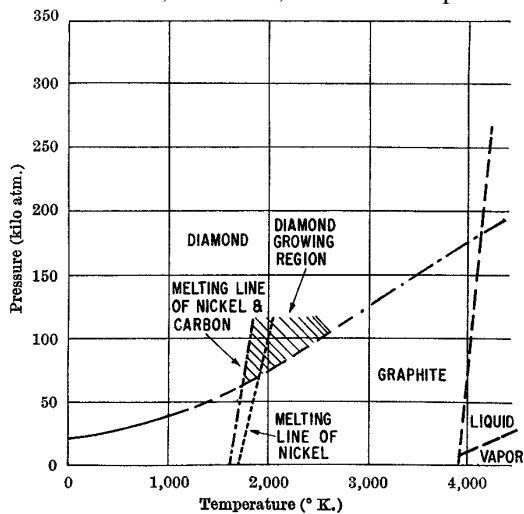

Fig. 7. Diamond-growing region

programmes will not permit any diamond to form from iron--carbon mixtures.

Shortly afterwards, a mixture of iron-rich iron sulphide together with carbon and tantalum, as shown in Fig. 5, was heated at about 1,600°C. at about 95,000 atm. The heating time was short, less than 10 min. On the tantalum end disks there formed tantalum carbide, and on top of this lay a black crusty layer of small diamond crystals (Fig. 6). They were identified by their hardness, combustibility and X-ray diffraction pattern. The experiment was successfully repeated many times.

Soon other substances were found to be effective as catalysts for the conversion of carbon into diamond at pressures ranging from 55,000 to 100,000 atm., and temperatures ranging from 1,200 to 2,400°C. They were chromium, manganese, cobalt, nickel, palladium, platinum, etc., or compounds which would react to give the free metals under these conditions, for example, nickel oxide, ferric chloride, etc.

After many experiments it became possible to list some of the conditions peculiar to the formation of diamond.

(1) The pressure and temperature of the system should be those for which diamond is thermodynamically stable.

(2) The temperature must be high enough to ensure that the catalyst metal, saturated with
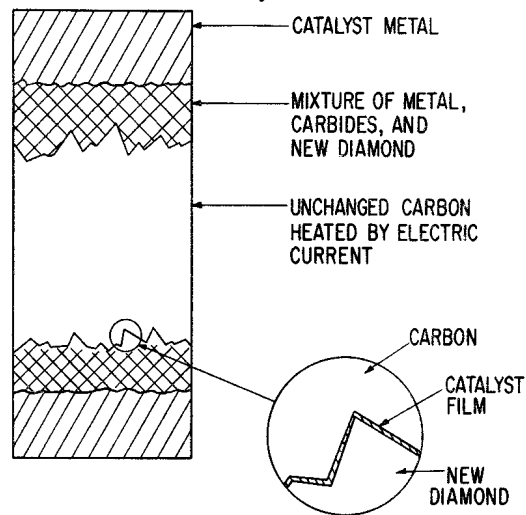

Fig. 8. Diamond growth from graphitic carbon

carbon, is molten. Thus the intersection of the melting line of the metal - carbon eutectic with the graphite - diamond equilibrium line sets a lower limit on the temperature and pressure which can be used to form diamond with a particular catalyst. In Fig. 7 the diamond-growing region is shown as a shaded area on the pressure temperature diagram.

(3) The catalyst metal can be chromium, manganese, iron, cobalt, nickel, ruthenium,

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rhodium, palladium, osmium, iridium or platinum. Tantalum is particularly effective for inducing the growth of small diamond crystals, although in some circumstances it may not be as catalytically active as the other metallic catalysts.

(4) New diamond can form whether

Fig. 9

diamond seed crystals are present or not.

(5) As the synthesis pressure and temperature are moved further into the diamond-stable region away from the graphite-diamond equilibrium line, the rate of nucleation and
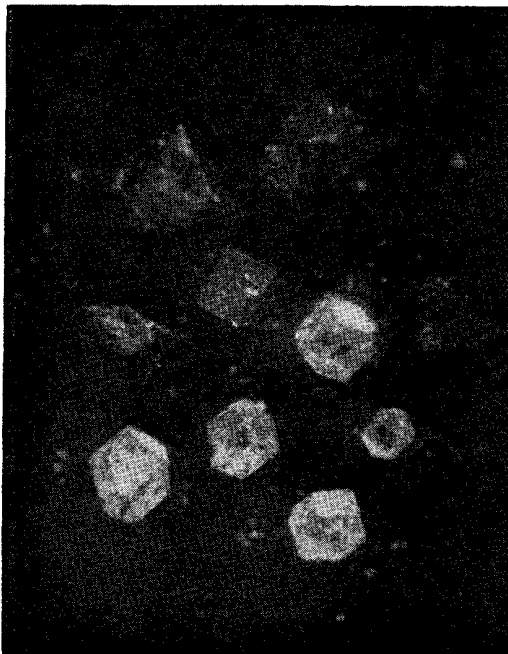

Fig. 10

growth of the diamonds increases and their average crystal-size decreases.

(6) The diamond can grow at very high rates, at least 0.1 mm. per min.

(7) The actual transformation from carbon to diamond occurs across a very thin film, about 0.1 mm. thick, which separates the carbon from the diamond. Thus the transformation is almost 'direct', but the catalyst is essential (Fig. 8). So far it has been found to be very difficult to grow diamond buried in molten catalyst even 1 mm. away from the source of carbon.

(8) Although the main driving force for the formation of diamond is the thermodynamic potential difference between graphite and diamond, temperature gradients can accelerate diamond growth due to the dependence upon temperature of the solubility of carbon in the catalyst.

(9) The kind of carbon used as a starting material has an effect on the kind and number of the diamonds formed. Good results have been obtained in making diamonds employing ordinary commercial graphite as the starting material. Other carbonaceous material may be
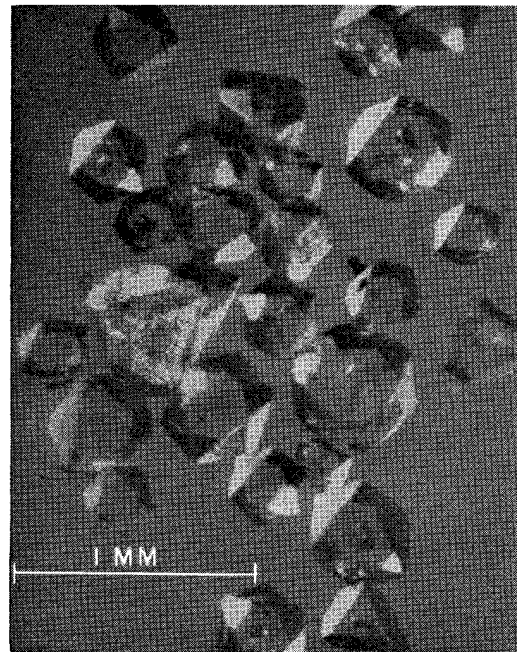

Fig. 11

employed as the source of carbon, such as carbon black or a sugar charcoal; but graphite is preferred.

(10) Sometimes graphite forms from a carbon-rich melt, particularly when the melt freezes, even though the pressure and temperature are appropriate for diamond stability. Diamond may or may not form at the

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same time. Apparently the formation of diamond is not a simple process.

(11) The diamonds easily include or grow around foreign particles present in the mixture, particularly at high rates of growth. Often some of the catalyst metal will be thus trapped in a diamond crystal.

(12) The diamond crystal habit varies according to the temperature of formation. Cubes predominate at the lowest temperatures, mixed cubes, cubo-octahedra and dodecahedra at intermediate temperatures, and octahedra at the highest temperatures. No tetrahedra have been found. At high growth-rates, octahedra are frequently twinned through an octahedral face as a mirror plane. Growth terraces or steps are common on the diamond crystals, but no growth spirals have been found so far. The colour varies from black at low temperatures through dark green, light green and yellow, to white at the highest temperatures. In many cases, the colour does not depend on the particular catalyst used but on the operating temperature relative to the melting point of the catalyst-carbon mixture. Green and yellow colours seem to be associated with imperfections in the diamond crystal lattice rather than with the presence of a specific impurity. Many of the physical characteristics of natural diamonds have been duplicated in the laboratory[vii].

Some photomicrographs of various synthetic diamond crystals are shown in Figs. 9-11.

[i] Rossini and Jessup, J. Res. Nat. Bur. Stand., 21, 491 (1938).

[ii] Berman and Simon, Z. Electrochemie, 59, 333 (1955).

[iii] Bovenkerk, Bundy, DeLai and Strong (unpublished work).

[iv] Williams, "The Genesis of the Diamond" (Ernest Benn, Ltd., London, 1932). Gubelin, J. Gemmology, 3, No. 5 (Jan. 1952). Wentorf (unpublished work).

[v] Bridgman, "The Physics of High Pressure", 424 (G. Bell and Sons, London, 1952).

[vi] Moissan, C.R. Acad. Sci., Paris, 118, 320 (1894); 123, 206, 210 (1896). Parsons, Proc. Roy. Soc., 79, 532 (1907); J. Inst. Metals, 20, 5 (1918); Phil. Trans. Roy. Soc., A, 220, 67 (1920).

[vii] Bundy, Hall, Strong and Wentorf, Nature, 176, 51 (1955).