

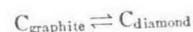
90 degrees to each other. This unit also operates on the principle of an extruded compressible gasket, although preformed gaskets similarly have been found to provide superior characteristics (see footnote² on page 1394).

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,



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,

$$\int_0^P \Delta V dP = \Delta F_{TP} - \Delta F_{T^0}$$

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.