

## Diamonds, Synthetic

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### Introduction

“And the second row *shall be* an emerald, a sapphire, and a diamond”; “Thou hast been in Eden the garden of God; every precious stone *was* thy covering, the sardius, topaz, and the diamond . . .”; “The sin of Judah *is* written with a pen of iron, and with the point of a diamond: *it is* graven upon the table of their heart, and upon the horns of your alters”—Exodus 28:18; Ezekiel 28:13; Jeremiah 17:1.

So says the Bible concerning diamond. The Exodus reference assigns 12 precious stones, including diamond, to be set in a breastplate worn by Aaron the high-priest. Each precious stone represents one of the 12 tribes of Israel. The Ezekiel lamentation affirms the precious nature of diamond, and the Jeremiah symbolism asserts that the sins of Judah were very bad and that diamond is very hard. The words of Jeremiah are the first known mention of an industrial use for diamond; namely, a scribing tool capable of writing on all other solid materials.

It is thought that diamonds of biblical times came from India, probably Golconda in Cashmere. However, diamond mining as an industry in India probably did not begin until about 700 B.C. The second source of diamonds is thought to have been discovered in Borneo about A.D. 600. Following this, diamonds were discovered in Brazil in 1726 and South Africa in 1867. Since that time, diamonds have been found in many places in Africa, and that continent remains to this day the world's principal supplier. Since World War II, diamonds have been mined in the Soviet Union. Diamonds were mined in the United States for a short time in Pike County, Arkansas, about the time of World War I. Recently, diamonds have been discovered along the Wyoming-Colorado border in the United States, but the extent of the deposit is not yet known.

The diamonds of India and Brazil and some of the deposits of Africa are alluvial. But the original source of diamonds is volcanic in nature. Hot lava of a peculiar nature had, in many parts of Africa, the USSR, and the United States, worked its way upward from great depths to the earth's surface. The resultant “pipes” of solidified lava contain a complex material known as “blue ground” and this is mined by

underground tunneling. The diamond content is very low. Only one carat (ct) of gem quality diamond is obtained from 320,000,000 ct of blue ground. However, 3.5 ct of industrial diamond is found along with the single carat of gem diamond. The geology of the pipes has been extensively studied. However, the manner in which the diamonds were formed in them is not known. The pipes offered no clues for the method by which diamonds were finally synthesized in the laboratory. The word carat comes from the carob bean which was used as a comparison of weight by the early diamond merchants of India. The exact weight of the carat has varied somewhat down through the ages, but is set today as being exactly equal to 0.2000 g.

The first extensive use of diamond in industry was as diamond powder mixed with olive oil. This abrasive slurry was placed on the horizontal face of a spinning cast iron plate to polish rough diamonds (held under pressure against the face) into faceted gems. The beginnings of this art are lost to history but probably started about A.D. 1500.

In the year 1927 a new, hard engineering material known as cemented tungsten carbide was introduced to the world. In this, micron-sized tungsten carbide particles are sintered together with cobalt powder to form a shape of the approximately desired dimensions. This rough shape is then ground to the precisely desired shape with diamond grinding wheels. A very important example of a diamond ground shape is the indexable tungsten carbide cutting tool insert. Throw-away inserts of triangular, square, and other shapes are used by the millions in various machine tools such as lathes and milling machines. A major use of industrial diamond today is in the grinding and finishing of various cemented tungsten carbide parts and cutting tools. As the tungsten carbide industry has expanded (growth has been remarkable since its introduction), the growth of the diamond wheel market has correspondingly increased. In 1935, only about half of all diamonds mined were used in industry. Now, this figure has increased to about 80%.

Before introducing the subject of industrial synthetic diamond and the methods for its production, it is appropriate to acquaint the reader with some of the properties of diamond.

### Properties of Diamond

Diamond made by man has only been known for 20 years. Consequently, most of the measurements that have been made to determine diamond's properties have been made on natural single crystals.

One classification of diamond originally based on its optical transmission properties can now be classed according to impurities that are present. Type Ia diamond contains nitrogen as an impurity in amounts ranging up to 0.2%. The nitrogen is located in relatively large sheets or platelets within the crystals, and most natural diamonds are of this type. Type Ib diamond contains nitrogen as an impurity but in a dispersed form throughout the crystal, and almost all synthetic diamond is of this type. Type IIa diamond has superior thermal and optical properties. These diamonds are very rare in nature and are free of nitrogen impurities and seem to have extraordinary crystal perfection. Type IIb diamond is extremely rare and has semiconducting properties. In addition, it is generally blue in color. Up to 100 ppm aluminum has been found to be present in Type IIb diamond. Semiconducting properties can be imparted to synthetic crystals by the incorporation of impurities, notably boron.

Diamond is unique among gemstones in that it is an element. Ideally, diamond consists only of the element carbon. All other gemstones are compounds containing two or more elements. Most impurities in natural diamond occur as inclusions. Graphite is a frequently found inclusion. A total of 22 mineral species have been identified as inclusions in natural diamond.

The pycnometric density of diamond is  $3.515 \text{ g/cm}^3$  at  $25^\circ\text{C}$ . Calculation of the density from X-ray diffraction data gives a value of 3.515506.

The nature of diamond and graphite as the atomic level were not known until after the advent of X-ray diffraction techniques for the determination of crystal structures. Diamond was one of the earliest crystals studied and was found to consist of carbon atoms arranged in puckered hexagonal rings lying approximately in the 111 crystallographic plane. This plane is the natural cleavage plane of diamond. These sets of puckered rings may be regarded as being stacked one above the other in a sequence such that atoms in every fourth plane duplicate the position of atoms in the first plane. By analogy to close-packed structures, such a sequence in

designated as . . . abcabc . . . In this structure each carbon atom is surrounded by four others in the well-known tetrahedral angle of  $109.47^\circ$ .

The arrangement of atoms in a crystal of graphite is similar to that in diamond. Graphite consists of a parallel stacking of layers of hexagonal carbon rings. These hexagonal rings, however, are probably only very slightly puckered, if at all. The classical graphite structure has an . . . abab . . . stacking sequence; that is, atoms in alternate layers occupy equivalent positions. It is also possible to have an . . . abcabc . . . stacking of hexagonal carbon atom rings in graphite. As with diamond, the cleavage plane in graphite is parallel to the stacked layers but, as is well known, graphite is cleaved with extreme ease compared to diamond. The distance between all atoms in diamond is  $1.54 \text{ \AA}$ . The interatomic distances between the carbon atoms within a hexagonal graphite layer are all  $1.42 \text{ \AA}$ . Thus, within the hexagonal sheet, the carbon atoms are more tightly bound than in diamond. The individual planes in the graphite lattice, however, are far apart ( $3.37 \text{ \AA}$ ). The average distance between puckered hexagonal layers in diamond is  $2.05 \text{ \AA}$ . The bonding in diamond is covalent and is due to the formation of  $sp^3$  hybrid bonds. All the bonds are equal and are "aliphatic" in character. In graphite, the bonds between carbon atoms in the hexagonal rings have some double bond character. In terms of molecular orbital theory, the carbon atoms in the hexagonal graphite rings are bonded directly between the atoms with  $\sigma$  bonds and above and below the hexagonal sheet are delocalized electrons forming a  $\pi$  bond. At any rate, the entire layer or sheet of carbon atoms in graphite consists of a giant two-dimensional resonating macromolecule—a molecule that is aromatic in character. A cursory examination of the similarities in the two structures would lead to the conclusion that graphite would be readily converted to diamond simply by shortening the distance between hexagonal planes from the  $3.37 \text{ \AA}$  in graphite to  $2.05 \text{ \AA}$  in diamond. Of course, in this process the flat hexagonal rings of graphite would need to "pucker" in order to cause the atoms to conform to the diamond crystal lattice. The direct application of pressure, it would seem, ought to be able to accomplish this. The direct conversion of graphite to diamond has been accomplished in recent years, but the pressures required are more than twice that required in the catalytic conversion that will subsequently be described. In addition to the higher pressure, there seems to be a necessity to

“shock” the graphite either by using a transient heating pulse or a transient pressure pulse such as can be obtained with explosive techniques. The face-centered cubic lattice cell constant for diamond is  $a_0 = 3.567 \text{ \AA}$  at  $25^\circ\text{C}$ .

When diamonds are heated in air, a black coating begins to form at a temperature of about  $600^\circ\text{C}$ . This black material is best described as nondiamond carbon. There are myriads of forms of the element carbon that are neither diamond or graphite which can be described, in part, as containing both tetrahedral and double bonds. At a temperature of  $1000^\circ\text{C}$ , diamonds will readily burn in air and disappear. If a diamond is heated in a vacuum or inert atmosphere, graphitization will commence at about  $1500^\circ\text{C}$ . The rate of graphitization increases rapidly above this temperature.

With respect to resistance of chemical attack, diamond is not affected by acids at room temperature. However, oxidizing acids will slowly attack it at elevated temperatures. Oxidizing molten salts such as sodium nitrate will begin to attack diamond at temperatures of about  $400$  to  $500^\circ\text{C}$ . Diamond is also attacked at elevated temperatures by carbide-forming metals such as titanium, zirconium, tantalum, and tungsten. Certain other metals such as the Group A metals and manganese and chromium, when in the molten state, will dissolve diamond.

It is not generally recognized that diamond has the highest thermal conductivity of any solid. For example, at  $20^\circ\text{C}$ , a type IIa diamond has a thermal conductivity value of  $26 \text{ W deg}^{-1} \text{ cm}^{-1}$  compared to the corresponding thermal conductivity of copper of only 4. At a temperature of  $-190^\circ\text{C}$ , Type IIa diamond has the amazing thermal conductivity of 120. A lattice mechanism in diamond is primarily responsible for its high thermal conductivity. In copper and other metals, thermal conductivity is provided primarily by electrons. Diamonds are currently being used for heat sinks in semiconductor devices. The linear coefficient of thermal expansion at  $20^\circ\text{C}$  is  $0.8 \pm 0.1 \times 10^{-6}$  and at  $-100^\circ\text{C}$  it is  $0.4 \pm 0.1 \times 10^{-6}$ . In the range of  $100$  to  $900^\circ\text{C}$ , the coefficient changes from 1.5 to  $4.8 \times 10^{-6}$ , and Gruneisen's law is obeyed between about  $150$  to  $950^\circ\text{C}$ . The specific heat of diamond at constant volume and  $20^\circ\text{C}$  is  $1.478 \text{ cal g-atom}^{-1} \text{ deg}^{-1}$ .

At room temperature, the electrical resistivity of Type I and Type II diamonds is generally greater than  $10^{16} \Omega \text{ cm}$ . Type IIb

diamonds have an electrical resistivity at room temperature in the neighborhood of  $10^{10}$  to  $10^3$ .

The compressive strength is about  $10^{10} \text{ dyn cm}^{-2}$  compared to a theoretical value of about  $10^{12}$ . The tensile strength of diamond is about the same as its compressive strength. Young's modulus is about  $10.5 \times 10^{12} \text{ dyn cm}^{-2}$ .

As is well known, diamond is the hardest of all known substances. The Moh's hardness scale, used for years by geologists, is based on scratch tests and is number from 1 to 10, diamond being the hardest mineral on the scale and talc being the softest. The scale is practical between 1 and 9 but it is impractical in the region from 9 to 10. Consequently, modern hardness scales are based on indentation tests rather than scratch tests. The Knoop microindentation hardness scale measures the hardness of diamond to be around 8000. The next hardest substance, synthetically created cubic boron nitride, measures about 4000 on this scale while silicon carbide and aluminum oxide are in the vicinity of 2000. All these values are nominal inasmuch as indentation hardness varies with crystallographic direction.

The abrasion resistance of single crystal diamond also depends very much on the orientation of the diamond. For centuries, diamond craftsmen have known that a diamond crystal is easier to lap or polish one direction than in another. The lapping of facets on a gem-quality diamond is traditionally done on a cast-iron scaife resembling a phonograph turntable. The diamond crystal is held in a simple mechanism called the dop which is weighted to hold the crystal at the desired angle against the rapidly spinning plate. The diamond laps or polishes readily in some directions and not at all in others. These directions are spoken of as being hard or soft. The diamond craftsmen can identify markings on the surfaces of the diamond and determine the “grain” and the proper direction for easy lapping and also for sawing or cleaving the diamond. It has only been since about 1950 that scientific studies have been made concerning the abrasion resistance of diamond.

The abrasion resistance is related to internal crystal structure and has also been noted to be related to the coefficient of friction. The “hardest” direction in diamond corresponds to the direction of lowest abrasion, which is also the direction of the lowest coefficient of friction. Modern quantitative experiments designed to accurately measure abrasion resistance utilize a diamond grinding wheel; i.e., a grinding wheel in

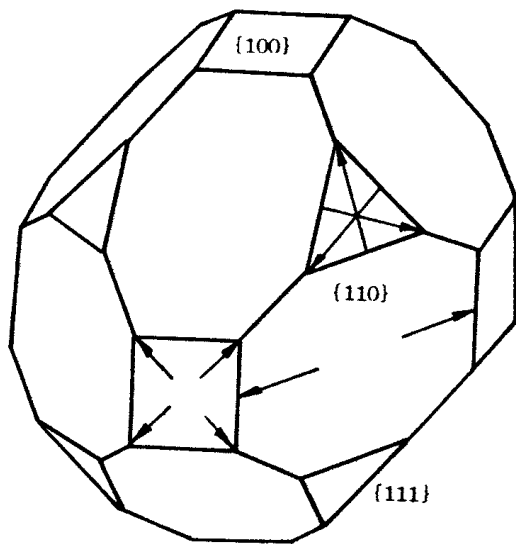


FIG. 1. Hard directions in diamond.

which the abrasive grain, diamond grit, is used to wear away the surface in a particular crystallographic direction. The diamond grinding wheel has a sharp edge and is applied to the diamond crystal under a given load and a specific direction for a specific length of time. The amount of diamond lost by reason of wear is then determined for each of the crystallographic direction in which the experiment is performed. Figure 1 shows the hard directions in diamond as measured by these abrasion resistance tests. The arrows indicate the direction of movement of the diamond wheel with respect to the diamond crystal and the 100, 110, and 111 crystallographic directions. The soft or easy directions are shown in Fig. 2. The abrasion resistance of diamond varies by at least a factor of 1:1000 depending upon orientation and direction of abrasion. Consequently, it is very important to orient diamond crystal utilized in tools to obtain the least amount of wear. This same orientation will also give the lowest coefficient of friction between the diamond and the work.

Scientific wear-tests, mentioned above, treat the diamond crystal "gently." In a practical application of the diamond this may not be the case, for diamonds may be subjected to impact loading. Diamond, like all hard substances, is strong when subjected to a steady load. But if a diamond is subjected to impact, it readily breaks. In many applications, impact loading cannot be avoided and "wear" of the diamond may result primarily from impact losses rather than the loss

in weight caused by normal abrasion. Cleavage of a single crystal diamond occurs readily along the 111 crystallographic direction. Consequently, this fact must be considered in the orientation of a single crystal for a particular tool application.

There have been occasions when claims have been made concerning the superior hardness of a new material to that of diamond. However, one can see from Fig. 1 that a softer substance oriented in its hardest direction might well be able to scratch the softest face of diamond if the abrasive test is performed in the correct direction. Such claims for a "harder" substance must be carefully scrutinized.

In an ideal sense, single-crystal diamond would have a perfect arrangement of carbon atoms throughout the entire macroscopic crystal. However, in a crude sense, diamond can be compared to wood. It has its natural grain along the 111 crystallographic direction and it also has knots. In diamond, the knots are called naaps. Naaps are caused by local changes in the arrangement of the carbon atoms. The knots in

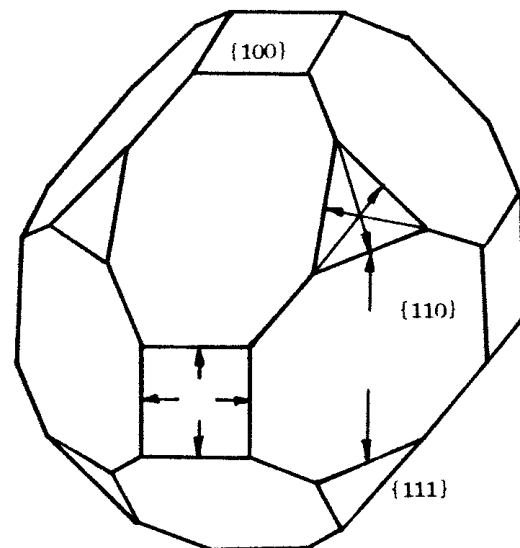


FIG. 2. Soft directions in diamond.

wood are usually tougher and harder than the main body of wood, and this is also the case in diamond. Someday it might be possible to synthesize diamond with naaps properly arranged to greatly improve the wear resistance and impact strength of diamond used for industrial purposes.

There is a naturally occurring diamond called carbonado. Its primary source is Brazil, although a small quantity also comes from

Africa. Carbonado is usually grey-brown or black in color. Sometimes it is glossy; other times it is dull and even porous, looking somewhat like the porous rock from volcanic lava flows. It occurs in nature only to the extent of about 0.15% of that of single-crystal diamond. Its wear resistance is only about 1/3 that of the average wear resistance of a properly oriented single-crystal diamond in a drilling or other abrasive type of application. However, it is much tougher and much more resistant to breakage by impact loading. Carbonado consists of diamond microcrystals no larger than 125  $\mu\text{m}$ . These microcrystals are oriented at random. Carbonado has not found extensive use as an industrial diamond because of its scarcity and because of the difficulty of shaping the material into a desired form. Single crystals of diamond can be shaped because of the natural cleavage grain. However, when attempts are made to cleave carbonado, unpredictable sizes and shapes are obtained. The toughness of carbonado might be explained as follows. A fracture propagating along the grain of a microcrystal would be stopped when an abutting crystal grain, is encountered. Materials similar to carbonado have now been made by man and will be discussed later.

A second polycrystal material found in nature is known as ballas. This material is exceedingly rare, occurring only to the extent of about 0.01% compared to single-crystal diamond. Ballas is generally round, oft-times with a pearl-like luster, and is extremely resistant to abrasion in any direction over its entire surface. It is thought that the polycrystalline grains in ballas are arranged along radial lines emanating from the center of the sphere to its exterior surface. Thus a hard vector of diamond is always present to any abrasive action tangential to the sphere's surface. This is indeed a very valuable industrial diamond, but attempts to synthesize a duplicate of this wonder of nature have not been successful.

### History of Diamond Making

The first authenticated synthesis of diamond was made on December 16, 1954 by H. Tracy Hall. It should be noted that this synthesis was unique in several aspects when compared to prior claims. (1) The diamonds were grown in a very short time; 15 to 120 sec. (2) The yield was high; that is, a significant portion of the graphite starting material was converted so that the

diamonds formed could be seen by the naked eye without being separated from the starting material. Also, the diamonds, though tiny (up to 350  $\mu\text{m}$  across) were obtained in sufficient quantity to be felt and held in the hand and could be heard to "scratch" as they were drawn across a piece of glass. This perception of the diamonds by the unaided physical senses were remarkably satisfying. (3) Hundreds of crystals were grown, many of them intergrown with each other and some were twinned. This contrasts sharply with the way diamonds are found in nature. (4) The discoverer readily duplicated his successful experiment a dozen times, and a short time later the experiment was duplicated by others. (5) the process was immediately recognized as being commercially feasible; indeed, less than 3 years after discovery, diamond grit was being sold on the commercial market!

The successful synthesis by another person was accomplished by H. Hugh Woodbury on December 31, 1954. Additional confirmation of the synthesis was made on January 17 and 18, 1955 when Richard Oriani and H. Hugh Woodbury duplicated the original synthesis run three times each. These six runs were made in the presence of official witnesses to make certain that the process worked at that no chicanery was involved.

A photograph of some of the first diamonds is shown in Fig. 3, and the X-ray diffraction pattern proving that the material was diamond is shown in Fig. 4.

Prior to the first synthesis of diamond many had learned from high school science books that diamond could probably be made by subjecting carbonaceous materials to great heat and pressure. The same idea was also presented in "comic books" where Superman created the great heat and pressure by clenching a lump of coal in his fist. The idea that high pressure and high temperature would be required to transform lowlier forms of carbon into diamond was a consequence of geological studies of the South African diamond-bearing pipes. Another clue was the higher density of diamond (3.51) compared to graphite (2.25).

A sketch of some earlier attempts to make diamond follows.

Before one could scientifically attempt the synthesis of diamond, he would need to know something concerning its nature. One of the earliest attempts to ascertain the nature of diamond was made by G. Averani and C. A. Targioni of the Accademia del Cimento. During

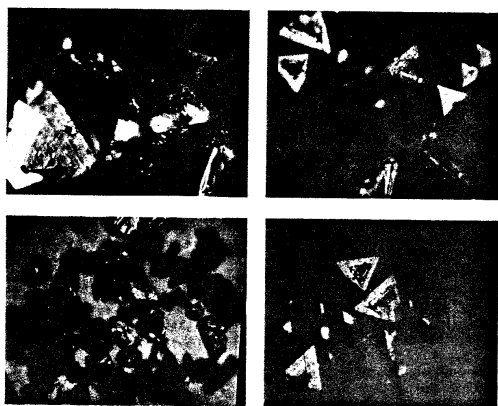


FIG. 3. The first synthetic diamonds.

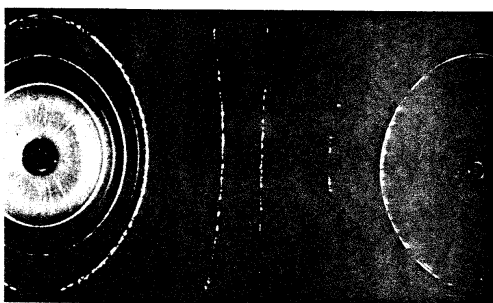


FIG. 4. X-ray diffraction pattern of first synthetic diamonds. Arrows point to diamond lines.

the years 1694 and 1695 they demonstrated that diamonds disappeared when heated in the focus of a large burning glass. They assumed that diamond evaporated under the influence of the high temperature. Today we know that diamond burned in the presence of the oxygen of the air and disappeared because it was converted into carbon dioxide.

In 1704 Sir Isaac Newton indicated that "a diamond is probably an unctuous substance coagulated," whatever that means. S. Tennant was the first to demonstrate that diamond is composed exclusively of carbon. He did this in 1797 by burning the diamond in a fused nitre bath and collecting the carbon dioxide that was formed. He also burned graphite in the same kind of fusion experiment and showed that equal weights of graphite and diamond formed the same quantity of carbon dioxide. L. B. Guiton de Morpeau also concluded that diamond and graphite are both carbon from an interesting experiment in which the diamond was heated with iron. He noted that the iron was converted into steel just as occurs when ordinary black carbon or graphite is dissolved in iron. As soon as chemists knew that graphite or ordinary black carbon and diamond were both composed of the

same elemental substance, they became interested in converting the inexpensive material into the other. If the common carbon of commerce could be turned into diamond, a millionfold increase in the value of the starting material would be obtained. There was, in addition, the interest of the scientific achievement. The earliest claim of success (C. Cagniard de la Tour) was made in the year 1823. In the 150 odd years that have passed since that time, the diamond synthesis problem has attracted the interest of thousands. Those pursuing the problem have ranged from charlatans through rank amateurs to the world's greatest scientists. Included among the great are Boyle, Bragg, Bridgman, Crookes, Davey, Despretz, Friedel, Liebig, Ludwig, Moisson, Parsons, Taman, and Wohler.

The literature on diamond synthesis is not very extensive. Most of the work has gone unpublished. Many of the world's large industrial organizations have considered the problem and have spent millions of dollars. So many years passed without success that those working on the problem felt embarrassed to admit that they were so engaged. Another aspect of the problem was the chicanery and fraud. Quite a number have claimed to possess a procedure for converting graphite into diamond, invited the unwary to invest their money, and then vanished.

Old school books and encyclopedias give credit to Henry Moisson as being the first to synthesize diamond. His work began in 1893 as an outgrowth of his invention of the electric arc furnace. He claimed to have made diamonds from sugar charcoal by dissolving this substance in molten iron and then rapidly cooling the molten mass in water. He thought that iron expanded on cooling and that the interior, which cooled more slowly than the surface, would, upon solidification, be subjected to great pressure. However, iron contracts upon cooling and it is not possible that any pressure was developed. Upon dissolving the mass in hydrochloric acid, Moisson thought he obtained small quantities of microscopic diamonds. Many workers, including Sir Charles Parsons (Parsons spent over 30 years and a fortune in attempting to produce diamonds) repeated Moisson's experiments without success. Parsons was of the opinion that Moisson has produced some chemically-resistant spinels from impurities present in the iron and that he had mistakenly presumed this material to be diamond.

J. B. Hannay said that he made diamonds in 1880 by subjecting wrought-iron tubes containing a mixture of bone oil, mineral oil, and lithium metal to a high temperature. Hannay claimed to have found a total of three rather large diamonds in two of the tubes that remained intact, some 80 tubes having exploded in his experiments. Again, no one else has been able to duplicate these claims. Interestingly, Hannay's diamonds may be seen in the British museum, and British encyclopedias to this day give Hannay credit for being the first to synthesize diamonds.

Care must be taken in diamond synthesis experiments to establish suitable criteria for determining that diamonds have been made. In the literature of diamond making, subordinates have confessed at a later date to having placed natural diamonds in the recipe from which the unsuspecting scientist hoped to obtain diamonds. There always seemed to be practical jokers around who, given the opportunity, will "salt" the experiment with the natural article. In further consideration of the "human element," diamonds have often been placed in the recipe by the scientist to "seed" the experiment and start diamond growth. There has been at least one instance in which a claim of synthesis was made where the scientist merely miscounted his seeds. At the end of the experiment he found one more diamond than he thought he had put in. Naturally he could not duplicate the experiment.

The amount of "diamond" material produced in most of the early claims was miniscule. The size of the particles was usually microscopic and identification was difficult because X-ray diffraction techniques were not yet available.

A diamond synthesis claim could only be genuine in light of (1) positive identification of the material as diamond, particularly by X-ray diffraction and chemical analysis. Adjunct identification could include observation of its density, index of refraction, hardness, crystal habit, and morphology. (2) The claimed process must be capable by duplication by the claimant and also by others!

An interesting note concerning secrecy in high pressure work and diamond synthesis has been given by David T. Griggs who, until his recent death was professor of geophysics at the University of California, Los Angeles. Professor Griggs was a junior fellow at Harvard (where Percy W. Bridgman spent his entire professional career) from 1934 to 1941. In a 1954 article Griggs stated, "It was my privilege to work in

Bridgman's laboratory during the period when working pressures were increased from 20,000 to 100,000 bars (one bar =  $10^6$  dyn/cm<sup>2</sup> = 1.02 kg/cm<sup>2</sup> = 1 N/m<sup>2</sup> =  $10^5$  Pa = 0.987 atm = 750 torr = 14.5 lb/in.<sup>2</sup>). As each new apparatus was readied for trial, I noticed that Bridgman would become very secretive and brusque. During the first run, visitors were not welcome. I subsequently learned that in each case graphite was the first substance tried." Bridgman's career in high pressure lasted from about 1905 through 1955. For a few years prior to the entry of the United States into World War II, Bridgman received very large financial backing from a consortium of companies to support research on diamond synthesis. While he received the Nobel Prize for his work in high pressures in 1948, he never succeeded in making diamond.

### Thermodynamics and Kinetics

The chemical engineer must be concerned with two factors when desiring to produce a chemical change: thermodynamics and chemical kinetics. In the case of the graphite/diamond conversion, there is a simplification in that this is a change from one polymorphic form to another. Thermodynamics, which considers the relative energies of the reactants and the products, states that when the free energy of the reactants is greater than the free energy of the products, the relative energy  $\Delta G$  is negative and the reaction has thermodynamic permission to proceed. However, for the reaction  $C_{\text{graphite}} \rightarrow C_{\text{diamond}}$ ,  $\Delta G^\circ$  is + 692 cal/g-atom at 25°C and 1 atm, and the reaction will not proceed at this pressure and temperature.

These similarities between the crystal structures of graphite and diamond, already discussed, suggest that a moderate pressure would shorten the bonds between the graphite layers by the proper amount and cause the atoms to conform to the diamond crystal lattice. However, the "direct" formation of diamond requires considerably more pressure than anticipated.

The first direct synthesis of diamond from graphite (without the aid of a solvent-catalyst—to be discussed later), was reported by DeCarli and Jamieson in 1961. They synthesized 8  $\mu\text{m}$  diameter diamond particles directly from rhombohedral graphite by means of explosive shock in which pressure was estimated to reach 300,000 atm. The temperature achieved in the shockwave was not known. Their process was

commercialized and for a few years a grayish product containing about 12% oxygen impurity could be purchased at about \$4.00/ct.

Subsequent to DeCarli and Jamieson's synthesis, F. P. Bundy reported the direct conversion of graphite to diamond using pressures above 125,000 atm and transient temperatures in the 3000°C range. He found, under these conditions, that the graphite spontaneously collapsed to polycrystalline diamond. In this synthesis he used a very small belt apparatus (to be described later). The graphite served as its own heater, a capacitor discharge supplying the current. At the present time, commercial production of diamond by direct conversion in static apparatus is not practical.

To return to the thermodynamic and kinetic problems, thermodynamics does not give any information concerning the time required for a reaction to take place. There are many instances in which the  $\Delta G$  may have a large negative value, yet the reaction proceeds at an imperceptible rate.

Reaction rate theory is not nearly as well developed as the field of thermodynamics. However, theories and techniques for understanding the developed to the point where a little theory, coupled with appropriate experiments, can often point the way toward finding the means for increasing or decreasing the rate of a given reaction. For the reaction  $C_{\text{graphite}} \rightarrow C_{\text{diamond}}$ , Berman and Simon calculated  $\Delta G^\circ$  from measured heats of combustion, specific heats, compressibilities, and thermal expansions. The positive value for  $\Delta G^\circ$ , of course, indicates that diamond is thermodynamically unstable with respect to graphite, but diamonds have not been observed to transform into graphite by any visible amount over periods of hundreds of years under ordinary conditions. The reaction rate for this conversion, therefore, is very slow. At elevated temperatures, however, the transformation of graphite to diamond begins to proceed at an observable rate in the neighborhood of 1200°C at 1 atm. At this pressure and temperature  $\Delta G$  has increased to about +2400 cal, indication a decrease in the thermodynamic stability of diamond with increasing temperature. At absolute zero,  $\Delta G$  for the graphite-diamond transition assumes its lowest value of 580 cal/g-atom at 1 atm.

Pressure is necessary in order to bring the graphite-diamond reaction into a region where  $\Delta G$  is negative. The pressure required depends

on the temperature; the higher the temperature, the greater the pressure. Equilibrium is established when the free energy difference between the two allotropes is zero, i.e.,

$$\Delta G = \Delta H - T\Delta S = 0$$

The manner in which  $\Delta G$  varies with pressure at a given temperature is given by

$$\left( \frac{\partial \Delta G}{\partial P} \right)_T = \Delta V$$

or by

$$\Delta G_T^P - \Delta G_T^0 = \int_0^P \Delta V dP$$

where  $\Delta V$  is a function of both  $T$  and  $P$ . From these expressions, the free energy difference at any pressure and temperature may be expressed as

$$\Delta G_T^P = \Delta H_T^0 - T\Delta S_T^0 + \int_0^P \Delta V dP$$

Data are available for evaluating  $\Delta H_T^0$  and  $\Delta S_T^0$  to 1200 K. Evaluation of the integral, however, involves some reasonable approximations. The equilibrium dividing line between the graphite and diamond phases is approximately a straight line with  $T = 500$  K at 20,000 atm and 2250 K at 70,000 atm, Diamond is stable above the line.

At pressures below about 125,000 atm, graphite has not been observed to transform directly to diamond and, since the thermodynamic criteria for formation of diamond can be met in experimental apparatus below this pressure, it must be concluded that kinetic considerations are controlling in this region and prevent the transformation from taking place in any practical period of time. In this connection an investigation of the rate process that might be involved below 125 kbar is enlightening. Although diamonds have not yet been made by direct conversion in this region, graphite can easily be made from diamond. Studies of the reverse transformation can give, with certain assumptions, information concerning the reaction mechanism. Experiments have shown that high pressure retards the rate of transformation of graphite to diamond, and the theory of absolute reaction rates indicates for such a situation that

$$\log \text{rate} = \text{constant} - \frac{\Delta V^\ddagger P}{RT}$$



where  $\Delta V^\ddagger$  is the molar difference in volume between diamond and the activated complex (transition state),  $P$  is the applied pressure,  $T$  is the temperature, and  $R$  is the molar gas constant. Although experimental data are somewhat limited, a plot of log rate vs  $P$  leads to the conclusion that  $\Delta V^\ddagger$  is at least  $10 \text{ cm}^3$ .

The molar volumes of diamond and graphite are  $3.42$  and  $5.34 \text{ cm}^3$ , respectively and their difference,  $\Delta V$ , is only  $1.92 \text{ cm}^3$ . The activated complex, with a molar volume  $V$  of at least  $(10 + 3.42 \text{ cm}^3)$ , must be a very open structure. Interestingly, making the assumption that the transition state for the graphite-diamond conversion is the same for the diamond-graphite conversion, higher pressure leads to more favorable thermodynamics (a more negative  $\Delta G$ ), but at the same time leads to less favorable reaction kinetics. The increased pressure hinders the expansion of the reactants into the large volume of the activated complex. Thus reaction kinetics apparently have the upper hand in direct conversion at pressures up to the vicinity of  $125,000 \text{ atm}$ .

The above analysis indicates the desirability of taking the graphite lattice apart and replacing the atoms one at a time into a diamond lattice. This might be accomplished by means of a solvent. A solvent could conceivably dissolve carbon atoms from graphite as individual entities which could then migrate through the solvent and precipitate in cooler regions as diamond. It has been assumed that this is the process taking place in the diamond pipes, or at least in the regions below the diamond pipes in the South African kimberlite (kimberlite being the mineralogical name if the blue ground). Experiments show that carbon is somewhat soluble in kimberlite. However, graphite has been dissolved in kimberlite, other silicates, and in such substances as lead and silver at pressures as high as  $70,000 \text{ atm}$ , simultaneously with temperatures in the diamond stable region and has been precipitated but not as diamond. It has always come out of solution as graphite. This indicates that (at least in the pressure-temperature regions investigated) mere solvency is not enough. Other forces or agencies must be required that are probably catalytic in nature.

In the first successful diamond synthesis, diamonds formed on a tantalum metal disk when graphite and the mineral troilite were present. Some tiny diamond crystals found in meteorites are surrounded by a film of troilite. Hence troilite was chosen as a possible catalyst for converting graphite to diamond and it worked— particularly

in the presence of tantalum. However, tantalum was not present in the diamond-containing meteorites. It is now presumed that the minute diamonds found in a few meteorites are formed by the shock pressures and temperatures generated when the meteorite crashes to earth. The Canyon Diablo meteorite at Meteor Crater, Arizona contains diamond.

Since FeS (troilite) is known to be a nonstoichiometric compound, usually with excess iron, pure iron was substituted for the FeS and diamonds were also grown. Substitution of pure sulfur for the FeS did not produce diamond. Microscopic examination of the cell contents following a run with FeS or Fe disclosed that a blackish coating (removable by acid) covered the diamonds. This coating was probably iron. Carbon atoms, derived from graphite or metallic carbides formed in the reaction mixture, apparently migrate through this film and precipitate as diamond. Simple substitutions of other transition metals for the iron subsequently showed many of these elements to be efficacious in producing diamond. This was particularly true with nickel, but Cr, Mn, Co, Pt and other Group VIII elements are also effective. All these elements are solvents for carbon but, in addition, they must possess catalytic power for properly orienting carbon atoms so that tetrahedral bonds and, subsequently, diamond are formed. Consequently, these substances are called “solvent-catalysts.” The tantalum, or perhaps tantalum carbide, which formed in the presence of the carbon in early experiments seems to aid diamond growth and has a role that is not understood. In the years that have gone by since diamond was first made, there have been innumerable experiments performed using alloys of various metals to find the best catalyst-solvent for the synthesis of diamond.

One goal of these experiments is to find an alloy that will reduce the pressure and temperature required. As a practical matter, this will reduce apparatus breakage. Tungsten carbide components such as anvils are expensive, and any reduction achieved in anvil failure is very worthwhile.

Different alloys and impurity additions also affect the crystal growth. The size and shape of crystals, as well as the degree of perfection, are important. Different types of alloys may also affect the amount and type of inclusions of foreign material within the diamond crystals. In this connection, diamond grit for use in plastic-bonded wheels works best when it has a certain degree of friability. As the grinding wheels spin

at high speed in grinding a substance such as tungsten carbide, the sharp points of the tiny grit act as miniature cutting tools, removing minute chips of the substance being ground. In the process, these tiny points become worn and rounded, and the dulled cutting edges are no longer effective in performing their job. Frictional forces tending to pull the grit from the plastic bond are smaller on the sharp point than they are on the dulled point. Consequently, if the grit has the proper friability, it will break when the frictional force on the rounded edge becomes sufficient. When this occurs, additional jagged points and edges are produced which again are effective in performing their grinding task. By a stroke of luck, the first synthetic diamonds had a proper amount of built-in friability (due to inclusions, fissures, poor growth, etc.) and performed more satisfactorily in plastic-bonded wheels (sometimes called resin-bonded wheels) when grinding tungsten carbide than did diamond grinding wheels which utilized natural diamond. As a matter of fact, in some grinding operations the new synthetic diamond grit performed 100 times as well as natural grit. (Performance was based on the weight of tungsten carbide ground away compared to the loss in weight of diamonds in the grinding wheel.)

Since most of the grinding wheels manufactured are resin bonded, this situation started a minor revolution in the diamond grit industry. The producers of natural diamonds had to devise new means for selecting various types of grits to meet this challenge. While the new grit performed phenomenally in resin-bonded wheels, its performance in metal-bonded wheels was poor. In metal-bonded wheels a metallic matrix binds and holds the grits to the rim of the wheel. In a metallic bond a strong, blocky grit is desirable. Manufacturers have now learned how to make this kind of grit (it takes a longer growing period and the yield is low). Competition from manufactured diamond has also resulted in improvement of natural diamond materials by selecting specific types of grit for certain types of grinding operations. This constitutes one more example of the benefits of competition in improving technology, ultimately benefiting the consumer. More will be said about commercial diamond materials later.

### High Pressure/Temperature Apparatus

Three types of equipment are used in commercial diamond synthesis. All are the inventions of H. Tracy Hall. They are the belt, the tetrahedral press, and the cubic press. In the belt, Fig. 5, the central portion of the apparatus consists of a tungsten carbide die with a tapered entrance hole on the top and bottom surfaces. This die accepts a cell which is made of pyrophyllite. Pyrophyllite is a hydrous, naturally occurring aluminum silicate. The better grades of this material are mined in South Africa. It is gray in color and can easily be machined with standard machine tools. The material is resistant to heat and has a low thermoconductivity compared to metals. It also serves to transmit pressure and has appropriate frictional and extrusion characteristics to form a gasket between the die cavity and two conical punches which are thrust into the top and bottom portions of the die. The punches conform to the internal shape of the pyrophyllite cell within the die. The opposing punches are pushed toward each other by a hydraulic ram. The die and the punches are surrounded by compound steel binding rings which exert an inward thrust on the tungsten carbide. This is necessary to prevent the failure of the tungsten carbide by the tensile loads which develop as a result of the compressive loads.

Located within the pyrophyllite cell is a heater-sample tube. The sample tube may be of graphite or a high melting metal such as tantalum and is connected through a tantalum disk at each end to a current disk. The current disk makes contact with the tip of the carbide punch on each end of the cell arrangement. High current electricity is brought through the current rings, the current disk, and the sample-heater tube to heat the contents of the sample-heater tube. The advance of the punches causes extrusion and compression of that portion of the pyrophyllite cell that is caught between the tapering sides of the punch and the tapering internal shape of the die. This compression and extrusion device admits the generation of pressures beyond 100,000 atm in the belt device.

The sample-heater tube usually occupies no more than 25% of the total volume of the pyrophyllite cell assembly. In a commercial machine for diamond production, the circular diameter of the punch tips is approximately 1 in. The distance between the punch tips is about 1 1/2 in. Up to 25 ct of friable diamond grit can be made in an apparatus of this kind in a 5-min cycle. When the belt is used in continuous duty, the punches and the die must be cooled. This is

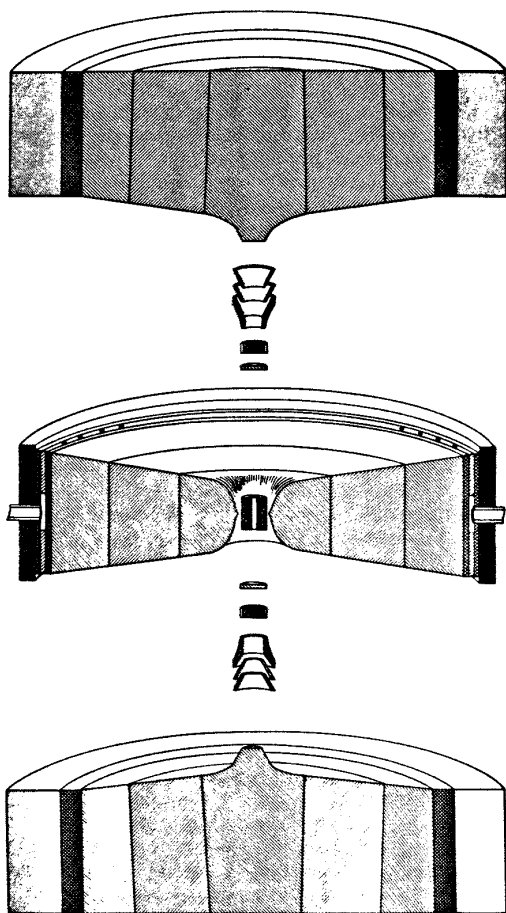


FIG. 5. The belt (schematic).

accomplished by placing water-cooling jackets around the binding rings which surround the punches and the die. The hydraulic ram that drives the punches in this commercial-size machine should have a thrust of about 1000 tons.

In the tetrahedral anvil apparatus, Fig. 6, four anvils, each having a triangular face and sloping shoulders which make an angle of  $35.3^\circ$  with respect to the plane of the triangular face, impinge in a symmetrical manner along tetrahedral axes upon a tetrahedral cell. The faces of the tetrahedral cell are triangular in shape and are larger in area than the corresponding anvil faces. After the anvils advance and contact the faces of the tetrahedral cell (which is made of pyrophyllite), additional anvil advancement causes pyrophyllite to extrude into the spaces between parallel sloping shoulders of the anvils. This automatically formed gasket, with continued advance of the anvils, compresses yields, flows, and extrudes, achieving a balance between frictional pressure

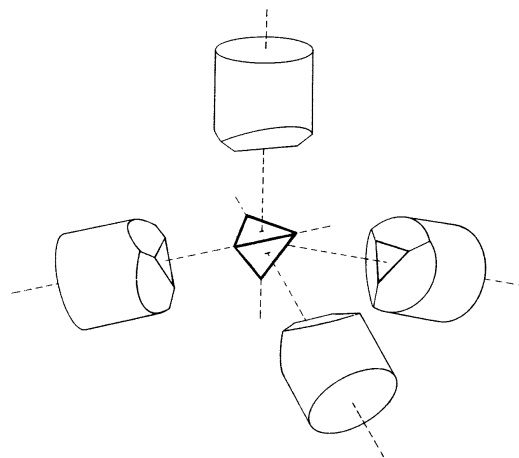


FIG. 6. Tetrahedral anvils and cell (schematic).

and other forces to form a seal and also providing pressure buildup within the cell.

Maximum pressures achieved in tetrahedral anvil devices are of the order of 140,000 atm. Routine, everyday pressures in commercial use are about 70,000 atm. A routine temperature simultaneously held with the 70,000 atm pressure is  $1800^\circ\text{C}$ . Both conditions can be simultaneously held for days. A tetrahedral cell is prepared from a solid pyrophyllite tetrahedron that is cut apart and drilled to provide cavities for the sample, electrical heaters, thermocouples, etc. as required. The assembled cell is held together by a small amount of white glue. All four tetrahedral anvils are electrically insulated from each other for making four independent electrical connections into the cell. As in the case of the belt, heating the sample tube is accomplished electrically (usually high current, low voltage). Figure 7 shows a tetrahedral press consisting of four hydraulic rams suspended in a tetrahedral frame comprising six tie bars fastened to four bases. The hydraulic rams provide the thrust for driving the anvils toward the geometrical center of the press frame. The anvils are synchronized in their advance and retract motion by an "anvil guide" system. The face of each anvil is always equidistant and symmetrically disposed with respect to the center of the press. The anvil guide consists of four guide plates, each one being mechanically integral with one anvil and its ram. The guide plates are positioned below the anvils, perpendicular to the ram axis. The ram axis passes through the center of the guide plate and the anvil. Each guide plate contains three guide holes symmetrically disposed around the ram axis at an angle of  $120^\circ$  to each other. The three

holes are also located at an angle of  $35.26^\circ$  to the ram axis. Also, each guide hole is aligned to be parallel with a corresponding press frame tie bar. The axes of all guide holes outline the six edges of a tetrahedron. Six guide pins are placed within the guide holes and interconnect the four guide plates. The guide pins are free floating and are of such length as to allow advance and retraction of the anvils over the required range without impeding full advance and without falling out of a guide pin hole when the anvils are fully retracted. When the anvils are advancing, the outline of the guide pin center line axes is a tetrahedron that is decreasing in size. When the anvils are retracting, the outline is increasing in size.

The cubic press, Fig. 8, is an extension of the tetrahedral anvil press idea. In a cubic press, six cubic anvils are directed along the axes of the Cartesian coordinate system to impinge on a cube of pyrophyllite. As in the case of the tetrahedral cell, the cubic cell is drilled and machined to accept appropriate components for bringing in heating current, for containing the sample, etc. The cubic anvil has a square face whose area is less than the area of the corresponding face of the cubic cell. The sloping sides of the cubic anvil make an angle of  $45.0^\circ$  with respect to the plane of the anvil face. In high-pressure machines of the tetrahedral and cubic type, a hardened steel binding ring is interference fit to the cylindrical surface of the tungsten carbide anvils. These binding rings provide an inward thrust toward the axis of the anvils and increase their life. The six electrically isolated cubic anvils provide six independent electrical connections to the interior of the cell. In all three devices (belt, tetrahedral press, and cubic press) the cell is used only once. The maximum pressure for routine runs with good anvil lifetime in the cubic press is somewhat lower than in the tetrahedral press; namely, 65,000 vs 70,000 atm. However, the cubic cell is somewhat more convenient in its geometry than the tetrahedral cell. It is obvious that the multianvil press concept (tetrahedral and cubic presses) can be extended to include octahedral presses, prismatic presses, and higher order geometrical configurations involving a greater number of anvils than six.

The pressure generated in the devices just described is directly related to the hydraulic oil pressure on the rams. A pressure calibration is made by imbedding a "pressure fixed-point wire" in a slug of silver chloride which is substituted for the sample in the cell. Wires of

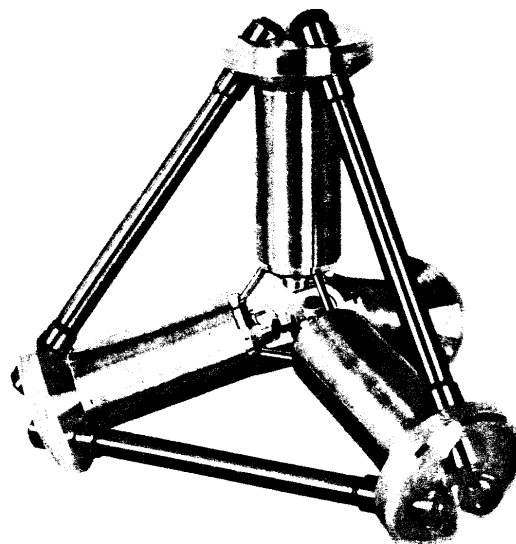


FIG. 7. A tetrahedral anvil press.

bismuth, thallium, and barium have discontinuities in electrical resistance (due to phase changes) as follows: Bi I-II, 25.5 kbar; Tl II-III, 36.7 kbar; Ba I-II, 55 kbar; Bi III-IV, 77 kbar. These wires are connected through the anvils or conical punches to a low resistance ohmmeter, and their electrical resistance is recorded as a function of oil pressure. A plot of the fixed-points vs oil pressure constitutes the pressure calibration for the apparatus. Calibration is made at room temperature and only with increasing pressure. Hysteresis of the pyrophyllite causes the fixed-point transitions to occur at a much lower oil pressure as oil pressure is reduced from a higher to a lower value. Although the calibration is made at room temperature, it is assumed to be approximately correct at high temperature. A decrease in the volume of pyrophyllite as permanent phase changes take place at high temperature tends to offset an increase in pressure caused by the temperature expansion of other components in the system. No one has as yet been able to determine high pressures simultaneously with temperatures above  $600^\circ\text{C}$ . Temperatures of 1200 to  $2600^\circ\text{C}$  are used in producing various diamond products.

#### Detailed Procedure for Laboratory Diamond Synthesis

A 200-ton cubic press similar to that depicted in Fig. 9 is used. A 200-ton press is a machine in which the maximum thrust of each hydraulic ram

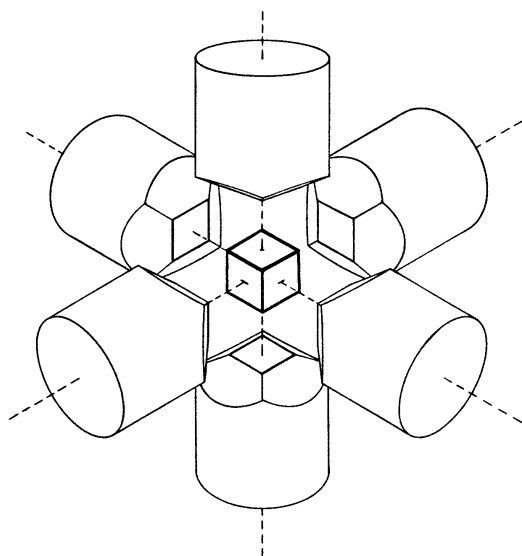


FIG. 8. Cubic anvils and cell (schematic).

is 200 tons. This particular press has hydraulic pistons of 8 in. diameter (50 in.<sup>2</sup> area) and operates on a maximum oil pressure of 8000 lb/in.<sup>2</sup>. The cubic cell is depicted in Fig. 10. The body of the cell is made of pyrophyllite, and the edge of the cube is 0.625 in., which is 25% longer than the edge of the corresponding square anvil face which is 0.500 in. The exterior surface of the cell is painted with a suspension of red iron oxide in water and is dried in an oven at 120°C for 0.5 h before use.

The central hole in the pyrophyllite is 0.250 in. in diameter and the counterbores on each end are 0.436 in. in diameter by 0.166 in. deep. The pyrophyllite thermal insulation plug located within the steel current ring is 0.333 in. in diameter by 0.166 in. long. The molybdenum disks at the bottom of each counterbore are 0.431 in. in diameter by 0.005 in. thick. The central hole of 0.250 in. is completely filled with alternating disks of graphite and pure nickel. The diameter of each is 0.247 in. The graphite disk thickness is 0.030 in. thick and the thickness of the nickel disks is 0.015 in. Graphite disks should abut the molybdenum disks on each side. A selection of nickel disks (0.005 and 0.010 in. thick) are kept on hand to add to the alternating stack as necessary to make the height of the stack sufficient to fill the sample space. This stack will serve as its own heating element in making the diamonds.

A paper tab about 3/8 in. wide and 3 in. long is attached to one edge of the cell with a small amount of white glue. When the anvils are in a retracted position, the cell is centered on the

lower anvil through which heating current will pass. One current ring should touch this anvil and the opposite current ring will touch the opposing anvil when the anvils are closed on the sample. The cell is held in place by placing a piece of adhesive tape across the paper tab onto the flat shoulder of the anvil's binding ring. Oil is then admitted to the hydraulic rams until the anvils contact the cell faces. Oil pressure is allowed to build up to 7000 lb/in.<sup>2</sup> which corresponds to a pressure of about 60,000 atm within the cell. During anvil advance (after contacting the cell), the 12 edges of the oversize cell (oversize with respect to the cube volume that would be enclosed if the anvils were allowed to touch with no cell present) will extrude between the sloping shoulders of the advancing anvils to automatically form a compressible gasket.

Once the cell is pressurized, heating current is applied. This current is supplied by a stacked-core type welding transformer for which the output voltage is controlled by a variable autotransformer connected to the primary winding. The electrical characteristics of such systems vary, so some experimentation will probably be required to select the correct autotransformer setting to obtain the proper temperature. For an initial trial, the Variac should be set for a current flow of 800 A through the sample. If the setting is correct, the current will start to decrease after about 20s of heating. As the current falls, voltage will rise. These combined signals indicate that diamond is being made. The temperature inside the cell is near 1500°C, the nickel is molten, and graphite is dissolving in it and crystallizing out of solution as diamond. Pressure is providing the thermodynamic driving force, and liquid nickel is acting as the solvent-catalyst.

The current falls as diamonds form because diamond is an electrical insulator while graphite is an electrical conductor (actually, diamond will be somewhat of a conductor at 1500°C). If the correct Variac setting is not found in the first try, new samples should be substituted for the old until the correct setting is found. If the initial temperature is too high, the sample is usually ruined as far as finding the diamond-making signal is concerned.

The current will probably level out near 200 A as diamond is formed. Heating power is disconnected after about 60 s. The sample will cool to room temperature is about 4 s. pressure is released after an additional 20s, at which time adjustments will take place in the cell and anvils

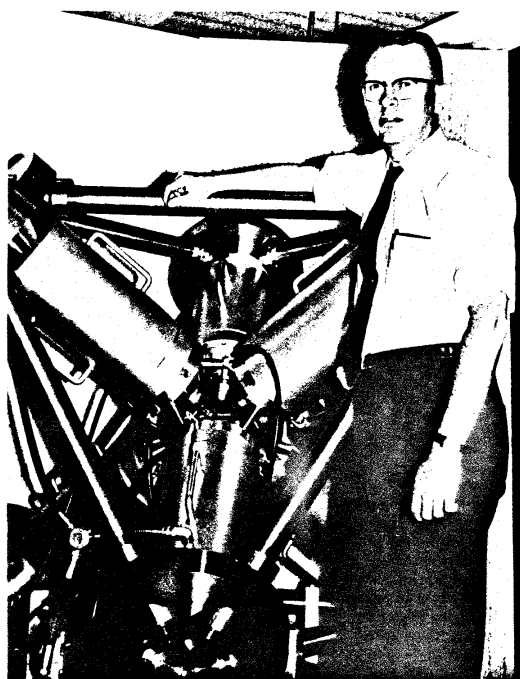


FIG. 9. A cubic press.

which will lengthen the anvil's life. The cell is now removed from the press and broken open with a hammer. The contents of the central hole can usually be retrieved as a cylinder consisting of a "welded together" mass of nickel, graphite, and diamond crystals. The pyrophyllite surrounding this cylinder will have been transformed into a white, hard ceramic containing kyanite and coesite. The diamond crystals can be retrieved from the cylinder by selective chemical oxidation.

The first treatment consists of concentrated  $H_2SO_4$  to which about 10% by weight of sodium or potassium nitrate is added. This mixture and the sample are heated strongly on a hot plate within a shielded fume hood for about an hour. When an appropriate temperature is reached, "clouds" of graphite particles will be streaming upward from the sample. Eventually most of the graphite is oxidized and disappears. At this point the liquid is carefully decanted and discarded. Following this, concentrated HCl is added to the sample and they are heated lightly on the hot plate. The HCl is then decanted and the residue washed with water. The diamonds will be clean enough at this point to be observed under 10 power magnification. Typical diamond morphological features will be evident. For additional cleaning, the  $H_2SO_4/NaNO_3$  and HCl treatments should be repeated until all the

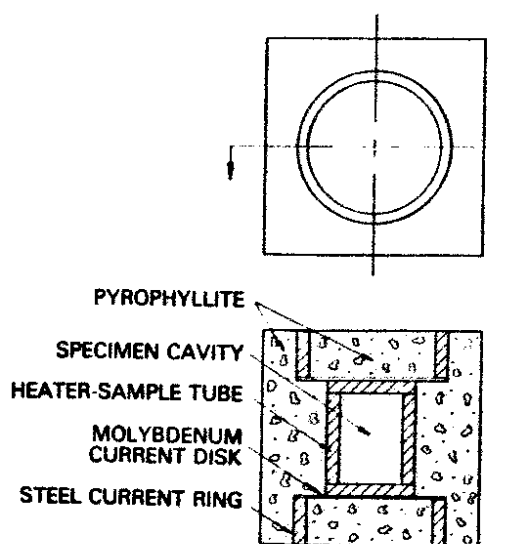


FIG. 10. Cubic cell (schematic).

graphite and nickel are gone. There will still be some residue from the pyrophyllite. This can be removed by prolonged treatment with concentrated HF solution or by fusion with  $NH_4F$ . The yield of diamond should be about 1 ct.

The diamond grit obtained can be used in a diamond grinding wheel. The color of the diamonds depends to some extent on the pressure, temperature, and time, and may range from black through yellow-green to transparent. Generally, higher temperature favors the formation of irregular, friable crystals.

Gem quality diamond of approximately 1 ct size was first prepared by H. M. Strong and R. H. Wentorf, Jr. in 1970. The starting material is diamond powder which is located in one end of a cylindrical sample chamber. A small diamond seed is located in one end of a cylindrical sample chamber. A small diamond seed is located at the opposite end, and a cylinder of nickel metal separated the diamond powder from the seed. The cell is maintained at a pressure near 57,000 atm and a temperature near  $1450^\circ C$ . At this temperature the nickel is a liquid. A temperature gradient is maintained in the cell so that the seed region is slightly cooler than the opposite end. The diamond powder slowly dissolves in the molten nickel and is transported to the seed where it is deposited. It takes 2 to 3 weeks to grow a 1-ct stone. Temperature and pressure must be carefully maintained at their proper values over this period of time. A good diamond

does now always grow; crystallization often goes “wild.” The process is far from economic at the present time.

### Industrial Diamond Products

Diamond grit is manufactured in the major industrial nations and annual sales are about \$150,000,000 (U.S.). The two major free-world producers are deBeers Industrial Diamond Division headquartered in England, and General Electric Specialty Materials Department located in the United States. A second United States corporation, Megadiamond Industries, is the third ranking producer. Grit sizes, depending on type, cover the range from mesh size (sieves in accordance with ASTM E-11) 25 to 400 and micron sizes from about +45 down to -10.

Many of the types of diamond have metal coatings, usually nickel or copper. The metal coatings serve a number of functions including strengthening the bond between the diamond and the wheel matrix. This keeps the diamond from popping out of the bond. Wheel performance (material removal rate) is also increased in many instances.

The manufacturers provide “tailor-made” synthetic diamond for three main uses: (1) grinding; (2) sawing and drilling; and (3) lapping, polishing, and fine grinding. In the grinding area, diamond is bonded to the wheel by resin (plastic) or by metal. In resinoid wheels, irregularly shaped friable crystals are best for grinding (wet or dry) nonferrous metals, particularly tungsten carbide. Metal-coated friable crystals tailored to wet grinding and to dry grinding of tungsten carbide and nonferrous metals are also available.

Metal bonding of diamonds to metal wheels or disks is accomplished by plating or by embedding diamond crystals in softer metals such as copper. Nickel is often used as the plating material for fine files and dental tools. Medium friability blocky crystals and nonblocky crystals find use here. Slightly elongated crystals of medium friability are best for some purposes.

Sawing and drilling require larger mesh sizes (which are expensive to produce), low friability, strong blocky crystals with a smooth surface. These diamonds are always bonded to the metal saw disk with metal. Such saws are used for cutting concrete, brick, stone, glass, and refractories.

The micron-sized powders are produced as friable and medium friable powders. They are

used as loose, nonbonded abrasives in lapping, polishing, and fine grading of carbides, refractories, diamond dies, gemstones, etc.

In addition to diamond grit, the major manufacturers synthesize cubic boron nitride (CBN), a material not found in nature and first synthesized by R. H. Wentorf, Jr. in 1957. It stands next in hardness to diamond. It is provided in several types as noncoated and metal-coated crystals. It is sold for the grinding of tool steels, stainless steels, and superalloys. Diamond does not generally perform well in grinding steels.

A synthetic diamond product akin to nature’s carbonado was first described by H. Tracy Hall in 1970. Diamond powder mixed with pure silicon as a sintering aid was subjected to pressures up to 80,000 atm and temperatures up to 2600°C in a refractory metal mold to produce circular, square, triangular, and other shapes of disks and cylinders.

This man made “carbonado” is lapped to provide precision, indexable cutting tools and wear parts, and has been commercially available since 1971. Recrystallized diamond containing cobalt was also introduced in the same year. Diamond powder and cobalt powder, mixed together, are subjected to a pressure/temperature regime where diamond is thermodynamically stable. The diamond powder dissolves in the molten cobalt and recrystallizes in a tightly bonded polycrystalline mass with cobalt occlusions.

A similar cobalt recrystallized diamond product about 0.020 in. thick bonded to a carbide substrate has more recently been offered for sale. A “wallpaper” coating of cobalt recrystallized diamond is also being applied to the inside of carbide dies and to the surface of other carbide tools with very good results.

The future is bright for continued improvement and innovation in the field of synthesized diamond products that outperform natural diamonds.

H. TRACY HALL