A HISTORY OF THE SCIENCE AND TECHNOLOGY OF DIAMOND SYNTHESIS

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After it was discovered in 1797 that diamond is a crystalline form of pure carbon, many attempts were made by chemists, physicists, and various kinds of inventors to synthesize diamond from other forms of carbon or carbon compounds. There were several claims to success, some of which were accepted for a while by the scientific community, but later disproved. The first truly reproducible process, openly announced in the scientific literature, was that of the General Electric Company in 1955. In the present paper, a brief historical background will be presented, including a review of the development of the scientific concepts that related to diamond synthesis, and the development of appropriate apparatus and processes.

EARLY SCIENCE

The discoveries, about 1800, by chemist Tennant and by chemist Lavoisier [1] that diamond is a crystalline form of pure carbon stimulated many experiments during the following 150 years to produce diamond from other forms of carbon, or from carbon compounds. As the science of thermodynamics began to develop in the later 1800's and early 1900's, it became evident that, thermodynamically, high pressure would favor the formation of diamond as compared to graphite. In 1901, Roozeboom [2] proposed a pressure/ temperature phase diagram for carbon which reflected qualitatively what was known at the time about the solid, liquid, graphite, and diamond phases. This was extended in 1909 by Tammann [3].

By 1938, the extensive and accurate work of Rossini and Jessup [4] on the heats of formation of CO_2 from diamond and from graphite, together with other experimental data on the compressibilities and thermal expansion properties of graphite and diamond, made it possible to calculate the difference of the Gibbs free energies of graphite and diamond as functions of pressure and temperature. From these calculations, a diamond/graphite "equilibrium line" could be drawn on a P,T phase diagram, based on zero difference of the free energies of the two forms. Points found for the equilibrium line were: 0 Kelvin, 13 kbar; 300K, 16 kbar; 470K, 20kbar. Experimental data for such calculations existed only up to about 900K. Extrapolations of the curve to higher temperature involved estimates of how the compressibilities and specific heats varied with higher pressure and temperatures. Workers like Bridgman [5], Leipunskii [6], Liljeblad [7], and Simon [8] made such extrapolations. Bridgman and Liljeblad reasoned that at higher temperatures, the equilibrium pressures would drop below a linear extrapolation, whereas Simon and Leipunskii argued in favor of a linear extrapolation. By 1951, the situation stood as shown in Figure 1 [9]. This diagram suggested that at temperatures high enough to produce practical reaction rates (i.e., ~1800-2000K) pressure in the range of 50-70 kbar would be required in order to be in the diamond stable region for a synthesis process.

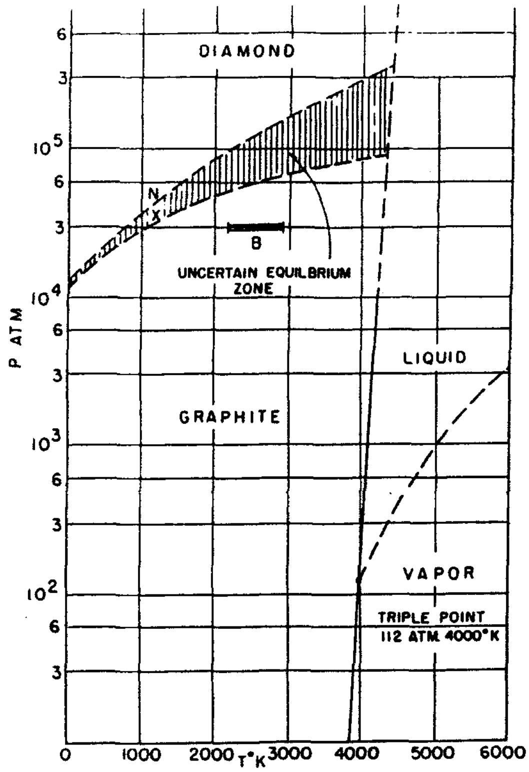

Figure 1. Composite diagram assembled by GE scientists in 1951 as a definition of the problem of synthesizing diamond. The lined region represents uncertainty in the equilibrium curve. The x under N is a datum point from Norton Co. The band marked by B is the region studied by Bridgman. The graphite melting curve is from Bassett.

From the point of view of thermodynamics, the Gibbs free energies of graphite and diamond are small compared to that of carbon vapor. Consequently, it would be quite possible (thermodynamically) for carbon vapor to condense

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as either graphite or diamond at low pressures. This was recognized in the late 1940's and early 1950's, and attempts were made to condense carbon vapor as diamond, rather than graphite, using "nucleation control." Such methods were not very successful until the 1980's when effective nucleation control methods were discovered.

In addition to having "thermodynamic permission" to go from a higher to a lower free energy state, A→B, the system usually has to pass through an intermediate state of higher energy, requiring an "activation energy." Early experiments and general observations showed clearly that the activation energies for phase transformations of carbon are very high, requiring very high temperatures to provide the necessary activation energy by thermal agitation. Thus, the known science indicated that, for the transformation of graphite to diamond, reaction systems involving relatively low activation energies should be sought in order to realize practical reaction rates at reasonable temperatures.

EARLY SYNTHESIS ATTEMPTS AND CLAIMS OF SUCCESS

The earliest attempts at diamond synthesis were mainly chemical in nature, and at atmospheric pressure. In the late 1800's the qualitative idea developed that diamond was a high pressure form since its density is greater than that of graphite (LeChatelier's Principle). Hannay in 1880 [10] reported experiments to form diamond in which he tried to reduce hydrocarbons and bone oil with lithium in sealed, thick-walled, iron tubes placed in a furnace at fairly high temperatures. Most of the tubes exploded disastrously. The contents of three or four of the tubes which survived yielded some very hard particles which appeared to be diamond. This result has been very controversial. Later, after x-ray diffraction analysis had been developed, it was determined by Bannister and Lonsdale [11] that the Hannay "diamonds" were indeed diamond, but of a rare type found in nature. Many concluded that the particles were "seed" diamonds put in with the initial reactants. No one ever succeeded in reproducing the experiments successfully.

Moissan in 1894 [12] reported successful synthesis of diamond by dissolving carbon in molten iron in an electric furnace at very high temperatures, and quenching this quickly as droplets in a quenching bath. The idea was the iron droplets solidified as a spherical shell which contracted as it cooled and compressed the inner liquid parts to high pressure causing the dissolved carbon to precipitate out as diamond and graphite. A few later experimenters reported successful results using variations of the Moissan process, but as x-ray diffraction analysis became available there were no instances of the hard particle products being diamond. Most of such particles were silicon carbides, which are quite hard and do contain carbon.

In a 1947 paper, Bridgman [5] described experiments on diamond and graphite at high pressure and temperature which explored the transformation of diamond to graphite and conversely. In the experiments, he succeeded in getting to pressures high enough to retard the diamond-to-graphite reaction at quite high temperature, but he never had any success in the graphite-to-diamond direction.

In a 1952 review, Eyring and Cagle [13] state that the scientific literature contained no certain example of the artificial production of diamond.

SYNTHESIS ATTEMPTS IN THE EARLY 1950's

From today's perspective it appears that by the early 1950's, the scientific world was about ready to accomplish synthesis of diamond under conditions of thermodynamic stability for diamond. Though not generally known at the time, it is now established that there were at least three serious laboratory programs with that goal. One was at the Norton Company in Worcester, Massachusetts, under Loring Coes. In a way, this was a continuation of an earlier project at Harvard University under Bridgman which was supported by the Norton Company, the General Electric Company, and Carborundum Company. A second project was in the ASEA laboratory in Sweden with Liander, von Platen, and Lundblad. A third project was at the General Electric Research Laboratory in Schenectady, New York, directed by A. J. Nerad, with Bundy, Hall, Strong, and Wentorf as workers. It turned out that the General Electric group was the first to accomplish a reproducible scientifically defined process which was publicly announced in the scientific and general literature, and was covered by appropriate patent applications [14]. The ASEA group announced later [15,16] that they had succeeded in synthesizing some diamond in 1953 but made no announcement because their apparatus was very cumbersome, the reactions were capricious and not well understood, and they were not aware of any serious competition. The Norton group claimed a sniff of success by 1951 and had shown evidence of their diamonds confidentially to certain academic persons before 1953. Much has been written about who made the first diamonds, and when. It may have been the Norton group or the ASEA group, but on the basis of reproducibility, scientific understanding and patent definition of the process, and formal announcement to the scientific and general community, the credit must go to the General Electric group. We note, however, that this Seminar is named as the 40th anniversary of diamond synthesis, which makes it 1953 - the year of the ASEA group.

SUBSEQUENT DEVELOPMENTS

Once diamond synthesis from graphite had been attained, understood, and tamed to a commercial process, some further developments followed rather naturally. First was the direct transformation of graphite to diamond without the aid of a catalyst/solvent. This transformation was first accomplished and reported by DeCarli and Jamieson [17] using shock compression of graphite. As the static pressure capability of "belt-type" apparatus was increased, Bundy [18] explored the melting point of graphite vs. pressure and eventually reached the triple point for graphite/diamond/liquid phases of carbon. In these experiments, using "flash" electrical resistance heating at very high pressure of over 120 kbar, the fast direct transition of graphite to diamond was observed to occur at threshold temperatures of about 3300K [18].

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A second development was the sintering of diamond powder into strong polycrystalline compacts for use as cutting tools and as wire drawing dies [19]. The fabrication of such compacts in which there is true and extensive bonding of adjacent diamond particles, diamond-to-diamond, proved to be very difficult and tricky, but a satisfactory process was eventually accomplished and such products became important commercially.

A third development was a process for growing large single crystals of diamond of high quality. To attain slow, controlled, high-quality crystal growth, it was necessary to go to a system that did not involve the graphite-to-diamond transition, because that process is very pressure sensitive. In a diamond-growing cell (high pressure/high temperature), temperature and temperature gradients can be much more accurately controlled than pressure and pressure gradients. The successful system [20] was polycrystalline diamond as the carbon "source" and a "seed" diamond as the carbon "sink," with the "source" held at a higher temperature than the "sink" in a bath of solvent metal held at a pressure well into the diamond stable region. In a properly designed and controlled system of this kind the carbon from the source can be made to transfer uniquely to the single growing seed crystal only. Single crystals of very high crystallographic quality can be grown by this method. The latest "fine-tuning" of this method has been to make the carbon source of isotopically pure polycrystalline diamond so that the large single crystal that grows from it is also isotopically pure [21]. Such crystals show a thermal conductivity at room temperature some 30-50% greater than similar quality crystals grown from nature's isotopic mix (~1% ^{13}C and 99% ^{12}C).

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