TESTING OF BURTON'S METHOD TO SYNTHESIZE DIAMONDS

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(ABSTRACT)

A method was investigated to synthesize diamonds at atmospheric pressure without the use of diamond seed crystals. The method was first proposed by Burton in 1905 and appears to have been lost in the literature. The procedure is based on Ostwald's principle of the formation of metastable, intermediate crystals en route to a more-stable final product. Carbon was dissolved in a lead-calcium alloy and was later precipitated out of the melt by the removal of calcium with steam. The calcium was used to increase the solubility of carbon in lead. Reaction temperatures between 775 K and 1025 K were used. The resulting precipitate, analyzed by both chemical and physical means, was found to be well-crystallized graphite. No diamond formation was found to occur.

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CHAPTER I

Introduction

The mystique surrounding the diamond has a long and eventful history. The diamond has been documented in history as far back as biblical times. It has been thought to cure the ill and protect against evil. It is the hardest of all naturally occurring materials. It is the peacemaker in matrimony and a sign of prosperity. Its mystery has prompted scientists to dedicate their careers to find out more about its nature.

In 1704, Sir Isaac Newton reported the refractive index of diamond as 2.439 (as compared to today's accepted value of 2.417). He speculated from this work that diamond must be combustible. In 1797, the English scientist Smithson Tennant burned a diamond in the presence of oxygen and found only carbon dioxide as a product (Mellor, 1946). It was concluded from this experiment that diamond was a second crystalline form of carbon, the other being graphite.

Daubree (1890) wrote that diamond was formed at great depths under the earth and its formation must therefore require high pressures and temperatures. In 1914, Damiens confirmed from thermodynamic experiments that diamond does indeed form at extremely high pressures and temperatures (Maillard, 1980).

During the past two centuries, scientists have exhaustingly attempted to convert the abundant and inexpensive graphite to the more precious diamond form. The most obvious approach to this problem has been to subject a carbon sample other than diamond to an environment of thermodynamic stability for diamond. The inherent difficulty with such an approach is the enormous pressures and high temperatures associated with the diamond-stable region. During the later part of the nineteenth century and the early part of the twentieth century, many claims of success were made but it is improbable that such rigorous conditions could have been obtained.

The most famous and controversial of the earlier attempts were those of Hannay and Moissan. Hannay's approach consisted of heating a mixture of bone oil, lithium and hydrocarbons in sealed wrought-iron tubes to a red heat (Flint, 1968). Upon quenching the tubes in cold water, Hannay claimed that diamond was produced. Moissan was inspired by the discovery of diamonds in an iron meteorite. He attempted to duplicate this phenomena by dissolving carbon in molten iron and subsequently quenching the mixture in molten lead (Holmes, 1960). By doing so, he believed that the great internal pressure produced from contraction of the cooling metal was sufficient to crystallize diamonds. Both Hannay and Moissan's work have been repeated countless times without success.

In 1955 Bundy et al. of The General Electric Corporation (Bundy et al. 1955) became the first to achieve a reproducible method to synthesize diamonds at high pressures. In a sense, they were the first to successfully build an apparatus which could sustain the enormous temperatures and pressures needed for thermodynamic stability. This was accomplished largely through the efforts of H.T. Hall and his belt pressure apparatus (Hall, 1958). The economic importance of such a discovery is seen from the fact that over two-thirds of the industrial diamonds used today are produced synthetically in a multimillion dollar industry (Nassau et al. 1979).

Since the General Electric discovery, many have succeeded in synthetically producing diamonds. Yet a problem associated with the high pressure technique is the lack of control of the reaction rate that determines the quality of the final product. Also inherent in the high pressure techniques are the enormous costs associated in obtaining the necessary pressures and temperatures (in the range of 35,000 to 100,000 atmospheres and 2000 to 4000 Kelvin). Though the procedure maintains economic advantages over mining and sorting, a process whereby diamonds could be synthesized at low pressures and temperatures would be much cheaper. In addition, low pressure diamond synthesis could provide the potential for better reaction control, thus enabling one to carefully manipulate the final product size and quality.

The quest for low pressure diamond synthesis techniques has been developing mainly since General Electric's success at high pressures. Prior to this time, mostly high pressure techniques were investigated. In 1962, a patent was granted to W.G. Eversole, of Union Carbide, for the metastable synthesis of diamond at low pressures. Eversole achieved his success by introducing diamond nuclei (in the form of seed crystals) to his sample. This promoted epitaxial growth of carbon on the surface of the seed crystals in the form of diamond. Since that time, metastable diamond growth on seed crystals has been successfully employed by many scientists. In all cases, the growth rates are found to be minute and, in addition, graphite formation eventually dominates.

The use of a diamond seed has proved to be the prerequisite for metastable growth. No successful attempts of metastable growth have been reported in the absence of a diamond seed. However, there was a claim to a low pressure method by C. V. Burton in the year 1905 that has been virtually ignored in the literature. The communication was discovered by Sebba (1982) from a reference to it in a book by W. C. Goodchild (1908). No other reference to this article has been found.

The communication, published in the London journal "Nature", discussed preliminary experiments by Burton for production of diamonds in a simple, yet ingenious, way that has some similarities to present day synthetic techniques. A reproduction of the original article appears as Appendix A of this report because of its relevance to the present study. There is evidence that Burton was a scientist of high standing so his communication should be taken seriously. A summary of some of his achievements is given in Appendix B.

Burton claimed that he produced diamond as a metastable form of carbon at atmospheric pressure and moderate temperatures. He reasoned that carbon would be precipitated from an alloy melt at low temperatures if a supersaturated solution of carbon was produced. Specifically, he stated that a small amount of carbon can be dissolved in a lead alloy containing one percent calcium. If steam is then used to remove the calcium from the alloy melt, carbon's extremely low solubility in lead alone will cause it to precipitate out in one of its allotropic forms. At temperatures in the range of 825 K to 975 K, Burton claimed that the kinetics were such that diamond was produced.

The remainder of Burton's communication presents the properties of the crystals produced as well as other possible methods which should be further investigated.

It is the present knowledge of the author that no one has attempted to verify the work of Burton until now. The purpose of this project was to try to reproduce the work of Burton and determine whether or not his claim was valid.

Because of the brevity of his initial communication, the experimental procedure is vague yet it provides enough general information to attempt to reproduce his work. The major points needing verification are his claim to have dissolved carbon in the lead alloy as well as his claim ultimately to have produced a metastable diamond product.

The goals of this investigation were:

1) To prepare a one percent calcium-in-lead alloy and determine the solubility of carbon in it.
2) To determine if diamond precipitates from the molten metal upon removal of calcium with steam.
3) To determine what form of carbon does precipitate if diamond was not produced in the former step.

CHAPTER II

Literature Review

Introduction

Techniques to synthesize diamonds in the laboratory are abundant in the literature. Prior to 1960, a majority of these techniques were directed toward high pressure methods. Since that time much attention has been devoted to metastable, low pressure syntheses.

The low pressure techniques all have in common the use of a diamond seed crystal to eliminate the difficult step of forming a diamond nucleus necessary for growth. This is in direct contrast to Burton's proposal. Methods of generating a supersaturated environment of carbon for metastable growth include chemical vapor deposition (CVD), ion-beam deposition and C+ ion implantation.

Burton's method involves the precipitation of carbon from an alloy melt. This approach is characteristic of the high pressure metal-solvent technique used today. Other high pressure techniques include shock-wave compression and static pressure conversion.

High Pressure Synthesis

It was mentioned earlier that the first successful and reproducible synthetic diamond process was devised by The

General Electric Corporation (Bundy et al. 1955). The solvent-catalyst process, as it is called, greatly reduces the pressure and temperature requirements necessary to obtain a diamond-stable region. A molten metal or alloy, particularly a group VIII transition metal, is used as a carbon solvent in the range of 35,000 to 70,000 atmospheres and 1700 to 2500 Kelvin (Bundy et al. 1973). A metal-carbide complex is said to be formed as carbon dissolves in the alloy. Upon saturation of carbon in the metal, the carbon precipitates out as diamond, the lower energy form under these conditions. The metal has been observed to form intermediate metal-carbide structures which maintain a low surface energy with diamond (Udoev, 1982). Thus the metal serves to lower the energy barrier necessary for diamond nucleation. Greater reaction control has been reported in which crystals as large as one carat could be synthesized (Wentorf, 1971 and Strong et al. 1971). The process required an exceedingly slow growth rate and, as a result, is tedious and expensive.

In addition to the metal-solvent procedure, diamonds have been synthesized without the use of metal solvents at exceedingly high pressures, in the range of 300 to 400 kilobars (Decarli et al. 1961). The high pressures needed are produced by shock compression waves. At these high pressures, graphite-to-diamond conversion is spontaneous.

The diamonds produced by this method are usually small, hexagonal crystals because of their rapid formation. Alder and Christian (1961) have also observed the spontaneous conversion of graphite to diamond under these conditions. Both the shock compression and metal-solvent techniques are currently used on a commercial basis (Kirk-Othmer, 1978).

A third method for high pressure synthesis employs the use of static pressures (Bundy, 1962). Graphite-to-diamond conversion was found to be spontaneous at pressures of about 130 kilobars and temperatures between 3300 to 4300 K. Diamond formation occurs within milliseconds at these conditions and is collected in the form of polycrystalline lumps. From this work, the triple point of diamond, graphite and molten carbon was estimated to be 130 kilobars and 4200 K (Bundy, 1963).

Low Pressure Synthesis

In 1962, W.G. Eversole filed a patent for the first low-pressure diamond synthesis technique (Eversole, 1962). He decomposed methane gas to supersaturate the vapor with carbon atoms in the presence of diamond seed crystals at 1320 K and less than one atmosphere. In his patent, he stated that,

> "The temperature and pressure of the invention must be such that the free energy potential of the carbon atoms in the gas is higher than the

> free energy potential of diamond carbon as well as graphite carbon. The free carbon system is then supersaturated with respect to both diamond and graphite."

A small growth of diamond was reported on the surface of the seed crystals as well as some graphite. The presence of the seed crystal was to eliminate the large energy requirement necessary for nucleation of the diamond phase. The energy barrier for diamond growth by extension of the crystal lattice was then less than that associated with graphite nucleation. Eventually, graphite growth overcame diamond growth. The process had to be stopped and the graphite removed before diamond growth could be continued. Further investigations (Hibshman, 1968) found that the presence of certain metals such as nickel, platinum and iridium accelerated the metastable growth process.

Derjaguin (1969) reported the synthesis of diamond whiskers by a method similar to that of Eversole's. An atmosphere of carbon tetraiodide gas was used as a carbon source at a temperature of 1275 K and a pressure of 0.00001 atmospheres. The gas dissociated upon contact with the heated seed crystals to produce a vapor with carbon atoms above equilibrium amounts. As in Eversole's work, graphite formation eventually overwhelmed diamond growth. Here, oxygen was added to the system at atmospheric pressure to oxidize the graphite (which oxidizes faster than diamond).

Growth rates equivalent to a three percent weight increase in a period of four hours have been reported (Derjaguin et al. 1975).

Several other investigators have successfully grown metastable diamond films on a seed crystal using carbon vapor deposition. It has been reported that the periodic addition of hydrogen gas at 50 atmospheres can remove 99.9 percent of the unwanted graphite while removing only 0.22 percent of the diamond (Angus et al. 1971). Growth rates as large as a 23 percent mass increase in a period of 25 hours have been claimed.

Fedoseev et al. (1980) have proposed that, although seed crystals seem to be necessary to induce metastable growth, it is theoretically possible to have homogeneous nucleation of diamond from a bulk gas phase. The necessary conditions are a high-enough supersaturation of carbon atoms and, "when the difference in chemical potentials between the gas and solid phases becomes much greater than the difference of chemical potentials between graphite and diamond" (Fedoseev et al. 1982).

Metastable diamond synthesis has also been accomplished by precipitation of carbon from molten metals (Brinkman et al. 1964). The method consisted of circulating a molten metal-carbon solution in an apparatus having both a hot and cool chamber that differ in temperature by approximately 525

K. A diamond seed was placed in the cooler region.

> "The essential condition is thus the contacting of a seed diamond with a molten medium in which the solubility limit of carbon is low, the molten medium being supersaturated with respect to diamond precipitation."

Metals that fulfill the above criterion include copper, silver, antimony, tin and lead. As the metal was circulated into the cooler region (where the solubility of carbon is lower than that of the hotter region), the carbon precipitated from the melt to form a thin film on the diamond seed. This film was found to be diamond. Similar experiments were performed by Merezhko and Skidanenko (1984) in which iron was used as the molten media.

Another method of metastable diamond growth was accomplished by an ion-beam deposition technique (Aisenberg et al. 1971). This method used no seed crystals. A thin film of carbon was deposited on such substrates as glass, silicon and stainless steel in both a crystalline and amorphous state. Upon impact with the non-diamond substrate, the high energy beam provided enough energy to overcome the energy barrier for diamond nucleation. The crystalline film was determined to be diamond-like by the presence of weak X-Ray patterns close to that of diamond. Growth rates were exceedingly small but the method was the first metastable technique not to use a seed crystal.

More recently, diamond growth on non-diamond substrates has been accomplished by carbon vapor deposition, CVD (Matsumoto et al. 1982). Here, the CVD technique was used to deposite microcrystals of diamond on such substrates as silicon, silica and molybdenum.

A new method for metastable diamond growth involves the use of C+ ion implantation (Nelson et al. 1983). Unlike other metastable techniques, success was achieved by internal growth of a diamond seed crystal. Bombardment with 10-20 Kev. of carbon atoms was able to penetrate well under the surface of the seed. A temperature of 875-1075 K was needed to provide enough mobility for atomic rearrangement (i.e. growth) within the crystal. Other workers (Freeman and Temple, 1984) have confirmed the validity of this method.

CHAPTER III

Discussion of the Feasiblity of Burton's Method

Introduction

Burton's synthetic diamond experiment raises many unanswered questions even with the chemical knowledge of today. His original communication mentioned several points without clearly stating the motives. Burton obviously understood the need for carbon supersaturation to facilitate nucleation. His use of a lead alloy shows sound judgement in view of the extremely low solubility of carbon in lead. He appears to have realized also the need to dissolve carbon in the substrate as free carbon or carbide. The communication also pointed out the negative results obtained when higher temperatures were used (i.e., graphite formation). All in all, Burton showed excellent insight of the necessary conditions for kinetic control of thermodynamic effects.

The theoretical aspects of Burton's work can be understood most easily from a kinetic viewpoint. Classical nucleation theory can be used to describe qualitatively the necessary conditions for metastable diamond growth. Other issues of concern are the nature of the lead-calcium alloy, the solubility of carbon in the alloy and the stablility of a metastable diamond product once it is formed.

The Properties of Diamond

Carbon exists as two crystalline allotropes, graphite and diamond. Other crystalline forms of carbon have been identified and appear to be intermediate structures between the two.

Figure 1 (Mantell, 1968) presents the crystallographic structure of both graphite and diamond. Diamond has a cubic structure in which each carbon atom is surrounded by four equidistant and adjacent atoms. The perfect symmetry and tight packing of atoms make diamond the hardest of all naturally occurring materials. A second crystalline structure of diamond that has been found to exist is of a hexagonal form (not shown in Figure 1).

Despite having the identical chemical composition of diamond, graphite, on the other hand, is widely used as a lubricant. The graphitic structure consists of planes of carbon atoms arranged hexagonally and attached to one another by weak interplaner bonds. As a result, graphite has a high tensile strength within a given plane whereas adjacent planes are relatively free to slide against one another.

Diamond maintains sp(3) covalent bonding whereas graphite exists with sp(2) hybridization. The cubic crystal structure of diamond belongs to the point group class Oh7. It is extremely brittle along the octahedral faces despite

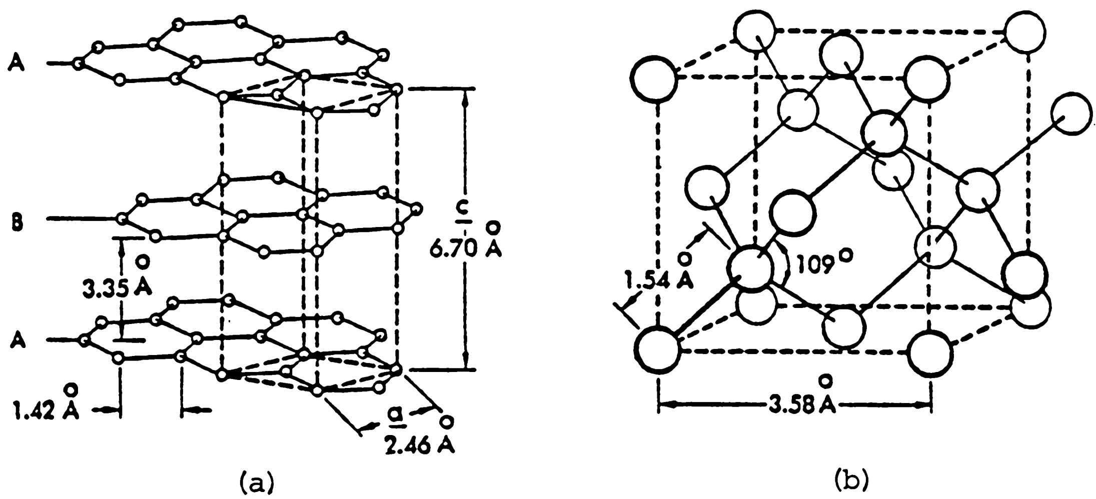

FIGURE 1.

Crystallographic Structure of (a) Graphite and (b) Diamond
(after Mantell, 1968)

its intense hardness. Diamond is chemically inert and is not attacked by acids such as hot concentrated sulfuric acid, nitric acid, hydrochloric acid and hydrofluoric acid. It readily oxidizes to carbon dioxide at temperatures over 1075 K and converts to graphite in an inert atmosphere at temperatures above 1570 K. The refractive index of diamond is 2.42 and its density is 3.41.

Phase Diagram of Carbon

In addition to the commercial importance of General Electric's synthetic diamond discovery, another implication of their work was a more accurate development of the phase diagram for carbon. Figure 2 (Bundy et al. 1962) shows such a diagram. Included in this figure are the approximate boundaries of the regions involved in the various diamond synthesis techniques. The liquid and metallic carbon boundaries shown in the diagram are only estimates derived from thermodynamics as such conditions have never been obtained experimentally.

Ostwald's Law of Successive Reactions

Thermodynamic equilibrium usually determines the final product in a transformation process. However, it is frequently observed during chemical reactions that a substance first appears as a metastable intermediate form

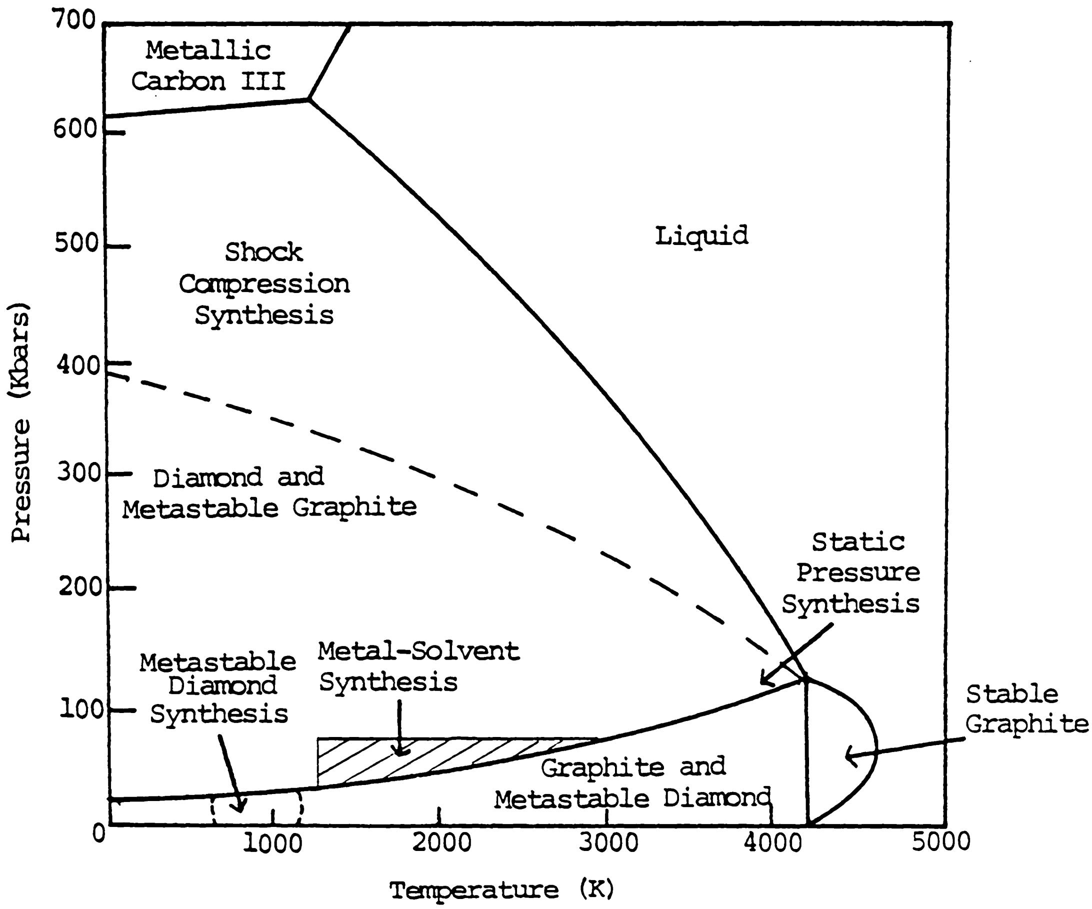

FIGURE 2.

Phase Diagram of Carbon
(after Bundy, 1962)

for a short period of time. Ostwald observed this phenomena and termed it "The Law of Successive Reactions." The "law" is not actually a law since many processes do proceed without the formation of an observable metastable intermediate.

Ostwald's principle can be generalized as, "When a substance is thrown out from solution, it is first deposited as a liquid or metastable crystalline solid, which later passes into the form stable at that particular temperature" (Findlay, 1951). Stated in a more modern tone, if a transformation proceeds from state "A" of higher free energy to state "C" of lower free energy, it may pass through an intermediate free energy form "B", if one such exists.

Examples of this phenomena are numerous in organic chemistry. 2,4-dibromoacetanilide, when crystallized from solution, first appears as expanded, needle-shaped crystals before forming a more stable and compact crystal structure when left in contact with the mother liquid (Chattaway et al. 1915). If removed from the solvent and placed in alcohol, the intermediate product can be kept for a period of years. Monoclinic sulfur can be produced in a metastable state at conditions where rhombic sulfur is the more stable form. Yellow mecuric iodide is observed as a metastable intermediate during the production of red mecuric iodide

(Findlay, 1951). There are countless other examples of Ostwald's "law".

All of these examples have in common the fact that the kinetics are such that the reaction proceeds slow enough to observe intermediate forms. It may even be that all reactions follow Ostwald's "law" but the kinetics are so fast that no intermediates are observable. This type of reasoning is the basis for Burton's method.

Nucleation Theory and Diamond Synthesis

There is an energy barrier associated with any transformation process. The forming phase must produce a decrease in the free energy of a system to occur spontaneously. Nucleation results in a decrease in free energy from the bulk phase while simultaneously adding energy due to the newly formed interface. Classical nucleation theory tells us that the growth of a new phase will occur only when the decrease in bulk free energy is greater than the simultaneous increase from interfacial surface energy (Nancollas et al. 1964). This corresponds to a nucleus of critical size.

Similarly, when carbon precipitates from a vapor there is a tendency for the system to decrease its free energy. There is an energy barrier present for both graphite and diamond formation. If one operates in the graphite-stable regime, graphite will be produced. However, if a nucleus other than graphite is artificially present, the equilibrium may be altered. Carbon vapor at low pressures has been shown to possess a free energy higher than that of graphite or diamond (Hibsman, 1968). Thus the work needed for growth on a diamond seed crystal (i.e., nucleus) might be less than that of graphite nucleation (Eversole, 1962). This alteration of thermodynamic equilibrium is the basis for metastable diamond growth employing the use of seed crystals.

But what if no seed crystals were present? Thermodynamics would clearly dictate the formation of graphite at low pressures. Burton's approach to this problem was to use temperatures at which the transformation of diamond to graphite is slow. Theoretically, carbon precipitating from a melt must pass through intermediate free energies on its way down to the lowest free energy form, that being graphite. If diamond falls within this intermediate range, a metastable state of diamond is feasible (in the spirit of Ostwald). It is then possible that the kinetics for the formation of diamond nuclei of critical size could be favored relative to the formation of critical graphite nuclei. The work of Brinkman et al. (1964) has shown that carbon precipitated from lead can crystalize as a metastable diamond film on diamond seed crystals (i.e., the free energy of carbon precipitated from lead is above that of graphite and diamond). Thus Burton's claim to have produced diamonds at metastable conditions in the absence of a seed might be valid.

Lead as a Solvent For Carbon

Of considerable importance in the above appoach is the initial state of the carbon dissolved in the lead-calcium alloy. For example, if carbon were present in the melt as a graphite-like structure (sp-2 bonding), then one would expect to precipitate graphite from the melt because of the increase in free energy associated with conversion to other forms. Burton implied that carbon dissolves in the alloy as free carbon or carbide.

No information has been found concerning the tertiary lead-calcium-carbon system. It is also unfortunate that the bonding character of carbon in lead or lead alloys is not discussed in the literature. Ruff and Bergdahl (1919) have reported carbon's solubility in lead at one atmosphere as 0.024, 0.046, and 0.094 weight percent at 1443, 1688, and 1828 K, respectively.

The use of lead as a carbon solvent at high pressures to facilitate diamond growth has been tried by Strong (1973) and Bakul et al. (1975). Strong tried lead as a solvent because the solubility of carbon in lead is of the same magnitude as that in copper-rich copper-nickel alloys (these alloys have been most successful as a solvent for diamond growth). It was found that only graphite crystallized from lead at 35-60 kilobars whereas lead-nickel alloys did produce diamond growth. He concluded from this observation that lead neither promotes nor poisons diamond growth. Bakul et al. found that lead was effective in promoting diamond growth at pressures above 60 kilobars. In addition, Russian scientists have claimed that lead catalyzed diamond growth at similar pressures (NSF, 1982).

As described earlier, Brinkman et al. (1964) have successfully used lead to facilitate metastable diamond growth. The lead was saturated with respect to diamond at a particular temperature and then channeled to a chamber of lower temperature. At this lower temperature, the melt became supersaturated with carbon and caused precipitation. As a result, a diamond film was deposited on a seed crystal. The solubility of carbon was given as 2.1 atomic percent at 1870 K and 0.05 percent at 1470 K. Lead was used for the same reason as in Burton's work: carbon's very low solubility in lead.

It is also of interest to note that diamond crystals have been prepared synthetically by heating graphite powder in the presence of calcium carbide at 2775 K and 90,000 atmospheres (Kuratomi, 1973). In addition, Ueda (1980) has shown that calcium carbide has a relatively low ability to enhance graphite nucleation. The relevance here is that the carbide might provide a low interfacial energy with diamond, as is the requirement for an effective metal solvent at high pressures. (Chernikov et al. 1983).

Oxidation of the Alloy by Steam

Burton used the removal of calcium as the driving force for carbon precipitation. Calcium readily reacts with water to form calcium hydroxide. Inherent in the use of steam to precipitate carbon is the ability to carefully control the the amount of supersaturation. Assuming that Burton did form diamond in this manner, larger crystal sizes may be produced by slowing the rate at which steam is admitted to the system.

During steam treatment, some lead oxide will be produced in addition to calcium hydroxide. It has been observed that lead oxides can oxidize graphite much more rapidly than diamond at 775 K (Kruse, 1967). Other workers (Szabo et al. 1978) have also shown that oxides of lead can react quite readily with graphite in an argon atmosphere. This might keep graphite nucleation to a minimum and subsequently prevent further growth of such a phase during the steam treatment in Burton's method.

Graphitization of Diamond

Numerous studies have been conducted concerning the graphitization of diamond. Although diamond is clearly the metastable form of carbon at ambient conditions, there is a significant activation energy associated with the transformation to graphite.

The rate of graphitization of diamond is negligible at temperatures below 1275 K (Phinney, 1954). The rate becomes significant only at temperatures greater than 1775 (Davies et al. 1972). The exact mechanism for the transformation has not been established fully although numerous theories have been proposed. Evans and James (1964) have used electron microscopy to show that the reaction proceeds at the surface of the diamond rather than internally. It is evident that such a transition would need some thermal excitation to break the tighly-held, covalently-bonded carbon atoms in diamond.

At temperatures higher than approximately 1775 K, the transition of diamond to graphite becomes appreciable. Many investigators have observed intermediate structures at the onset of the graphitization process. Pure diamond heated to 1875 K has given rise to electron diffraction patterns other than those of graphite or diamond (Seal, 1958). These new patterns were attributed to intermediate structures between graphite and diamond.

Assuming that carbon, precipitating from a melt, does pass through a metastable state of diamond in its transition to graphite, the low temperatures used in the "diamond-making" step would be insufficient to continue the transformation to graphite (of course, the oxidizing environment might aid somewhat in this step). Burton readily acknowledged that only graphite is produced at steam treatment temperatures above 1075 K. Though this temperature is somewhat low in light of the temperatures given above, Burton obviously realized the need to kinetically control the graphitization process by using lower temperatures.

Preparation of a Lead-Calcium Alloy

Lead-calcium alloys of extremely low calcium content (i.e., less than one percent calcium) have been used for some commercial applications. Lead with small amounts of calcium are found to have advantageous physical properties over that of pure lead. Such changes include increased hardness, excellent frictional properties, improved resistance to corrosion and increased tensile strenght (Aravamuthan et al. 1965). Commercial uses include cable sheathing, alloying agents and battery storage cells.

Figure 3 gives the phase diagram for the lead-calcium system (Elliott, 1965). Three forms of lead-calcium

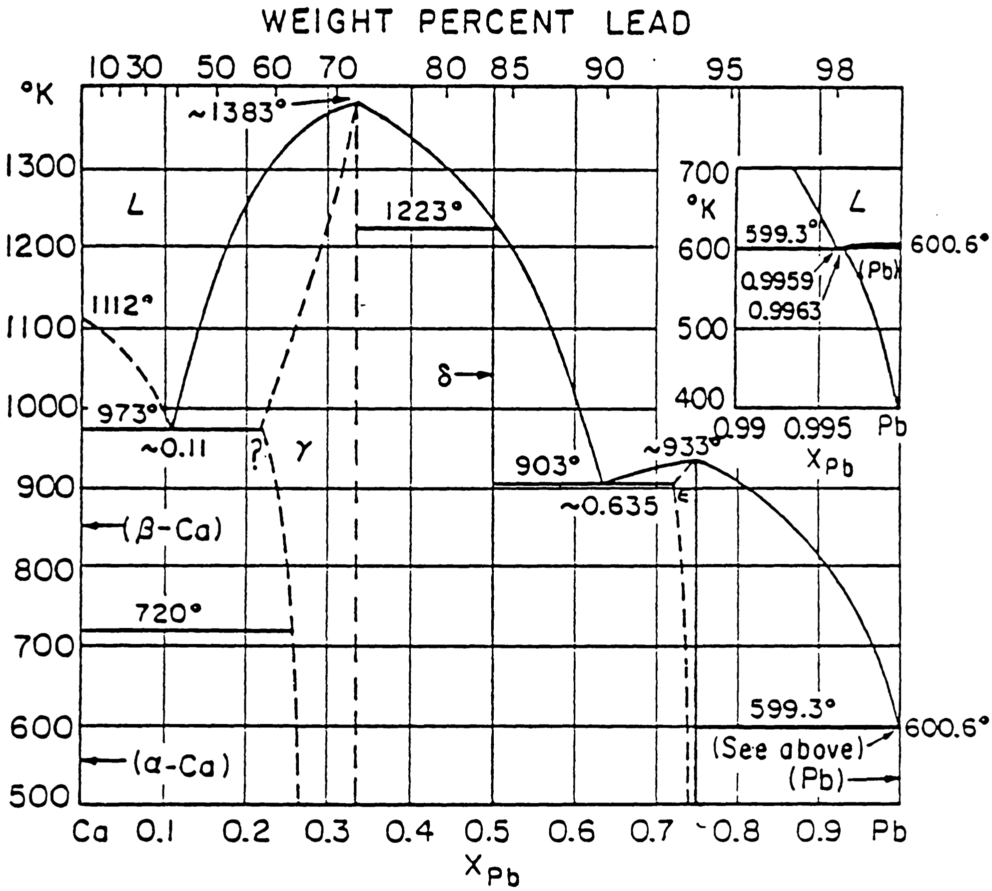

Figure 3.

Phase Diagram of the Lead-Calcium System
(After Elliott)

compounds have been documented in the literature (Muradov, 1967); PbCa, $PbCa_2$, and Pb_3Ca. Alloys of low calcium content (to the right on Figure 1) maintain the Pb_3Ca structure. The eutectic temperature has been verified to be 599.25 K as compared to the melting point of pure lead of 600.3 K (Vigdorovich et al. 1959). The alloy formation proceeds according to the reaction,

$$3Pb + CaC_2 \longrightarrow Pb_3Ca + 2C$$

where the carbon product has been reported as both graphite (Nashelskii, 1958) and an amorphous carbon (Yakoyama et al. 1951).

The above reaction proceeds by the dissociation of the calcium carbide (by electron transfer within the carbide) and the subsequent solution of metallic calcium in the lead. The dissociation reaction also generates very reactive carbide ions, C(2-), which will either stabilize by transforming to a lower energy form of carbon or dissolve in the lead. This point is of concern in the present investigation. It is felt that the free carbon atoms (or molecules) have a better chance of being absorbed into the metal than a more stable carbon form such as graphite.

Several methods of preparing lead-calcium alloys have been proposed in the literature. One method is through direct contact of pure calcium and lead metals (Muradov, 1967). Another method is to heat lead, calcium carbide and calcium chloride under a reducing atmosphere at 1270 K (Yokoyama et al. 1952). The chloride is used as a flux to aid in the dissociation of the calcium carbide. Other methods proposed usually include similar salts to promote carbide dissociation. Reducing atmospheres include the presence of carbon powder or aluminum.

The dissociation temperature of calcium carbide is approximately 2775 K at one atmosphere and substantially lower at higher pressures (Kosolapova, 1971). Thus a flux should be needed to aid in the dissociation at temperatures lower than 2775 K. Yokoyama reported that alloys of no more than 0.04 percent calcium could be prepared in the absence of a flux.

CHAPTER IV

General Experimental Method

Experimental Setup

Figure 4 presents a schematic diagram of the apparatus used in the experiment. All reactions performed in the experiment were carried out in a tube furnace made by Thermolyne Corporation (model # F-21120) of Dubuque, Iowa. The tube furnace was equipped with a built-in temperature sensor and readout in both Celsius and Fahrenheit. The maximum temperature obtainable was approximately 1475 K.

The furnace was equipped with a quartz tube made by the Chemistry Department Glass Shop at VPI. The tube was two feet long and 40 millimeters in diameter. Earlier experiments with alundum tubes were unsatisfactory due to the cracking of the tubes from thermal shock encountered during steam treatment. The inlet of the tube was fitted with a female connector equipped with a small opening used to introduce steam, nitrogen or argon. A second hole was used to introduce a thermocouple or stainless steel tube into the furnace. The steel tube was used to induce mixing of the melt in the reaction vessel by bubbling argon through it. The outlet of the tube was fitted with a water trap to observe gas flow rates and scrub any lead vapors emitted from the tube.

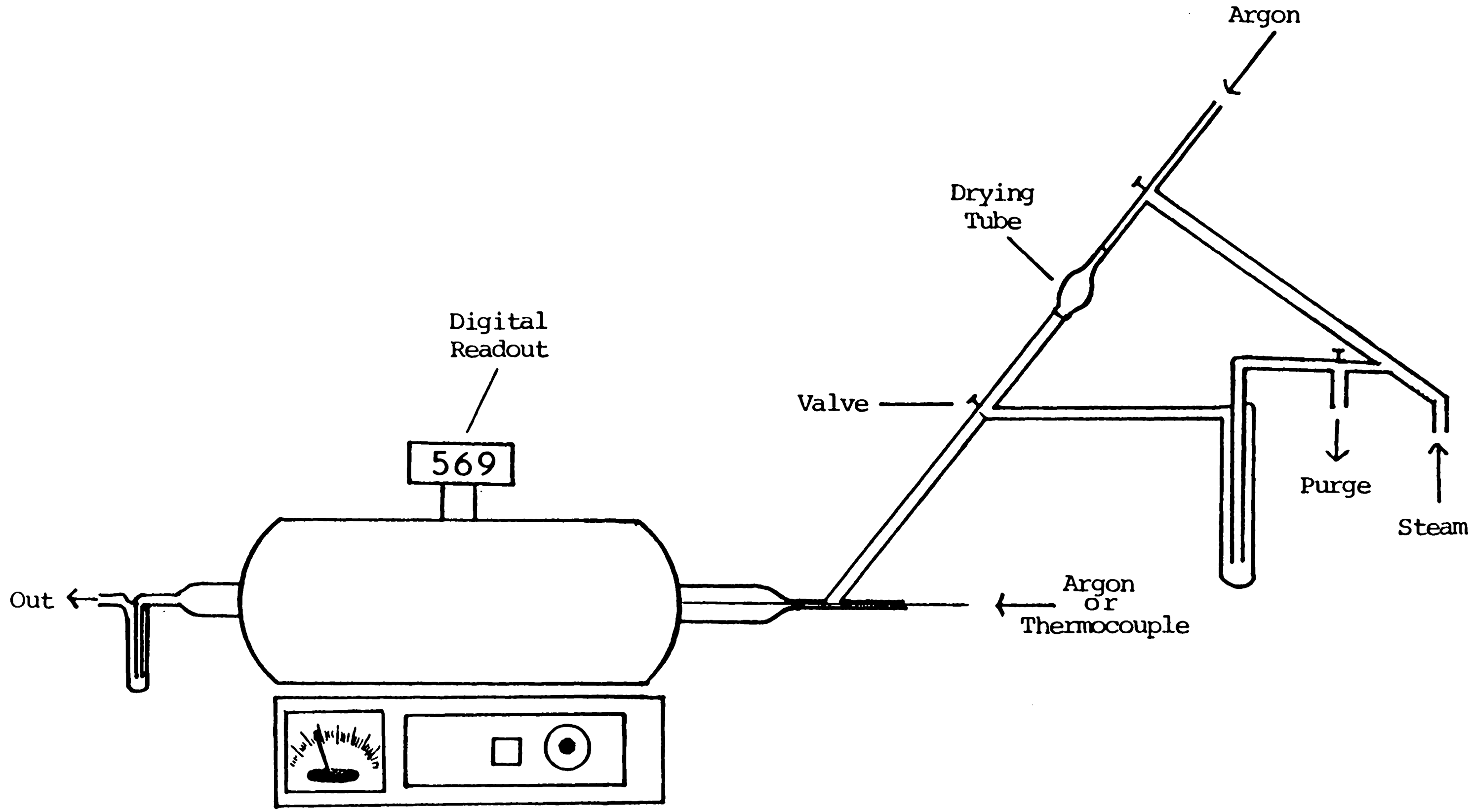

FIGURE 4.

Experimental Apparatus

The temperature, as recorded by the tube furnace readout, was corrected by calibration with a Type J thermocouple and digital readout (model # 400-J-C) from Omega Engineering, Inc. of Stamford, Conneticut. A calibration curve was made to compare the furnace temperature reading with the actual temperature recorded by the thermocouple.

Both nitrogen and argon were used to provide an inert atmosphere inside the tube furnace during reactions. Both gases were of a pre-purified grade and were supplied by Airco, Inc. of Montvale, New Jersey. A drying tube was placed in the gas line.

Steam used in the "diamond-making" step was generated by heating distilled water and mixing the resulting vapor with the gas flow line. The mixture was then passed through a steam trap to collect any condensed liquid. A valve was used to purge any air that might have been present in the steam line.

The reactions were carried out in both ceramic and graphite boats. The ceramic boats were manufactured by Coors Porcelain Company of Golden, Colorado. The graphite boats were made by the Chemical Engineering Department Machine Shop at VPI from blocks of fused graphite. The graphite boats were eventually the only ones used because of lead oxide and calcium chloride attacks on the ceramic.

A drying oven was used periodically in the experiments. The oven was a Lab-Line Imperial II made by Lab-Line Instruments, Inc. A Mettler balance (model # H33AR) was used to weigh samples. A Nikon Microscope (model # SC) was used to observe the final product collected.

Starting Materials

The chemicals used in the synthesis procedure are listed in Table I, which includes both the source and assay of each. The calcium carbide, used as a source of both carbon and calcium, contained approximately 20 percent impurities commonly encountered during its production. Pure calcium carbide was not available. Calcium chloride was used as a flux in the alloy preparation and, although labelled anhydrous, needed to be dried at 590 K before use. Graphite, charcoal and lampblack were used as possible carbon sources for the alloy. Nitric acid was used to dissolve away lead and calcium after the steam treatment.

General Procedure

Burton's diamond synthesis was reproduced in the laboratory. The original paper was vague in its experimental procedure as it was intended only as a preliminary announcement of the topic. Many problems of interest were encountered during the course of the

TABLE 1.

Chemicals Used in Experiment

Chemical	Purity (%)	Substantial Impurities	Manufacturer
Calcium Carbide	80	14% Calcium Oxide 2.3% Silica 0.9% Calcium Sulfide	Fisher Scientific New Jersey
Lead	99	----	"
Carbon Lampblack	99+	----	"
Graphite	98	----	"
Hydrofluoric Acid	49	----	"
Calcium Chloride (anhydrous)	98	----	Allied Chemical New Jersey
Nitric Acid	69-71	----	VWR Scientific San Fransisco

investigation. These problems were dealt with in a simple manner so as not to get side-tracked from the ultimate goals of the experiment.

A general outline of the steps involved in recreating Burton's experiment is as follows:

1) Prepare a one percent calcium-in-lead alloy in an inert atmosphere of argon.
2) Add carbon to the lead-calcium system with calcium carbide, lampblack, graphite or charcoal as the source.
3) Subject the resulting lead-calcium-carbon system to a slow flow of steam and argon at temperatures between 775 K and 1025 K to remove calcium and precipitate carbon from the melt.
4) Dissolve the product in nitric acid to remove the lead, calcium and other products formed during the steam treatment. Decant the solution and wash the residue thoroughly with water to remove any lead nitrate crystals.
5) Centrifuge the residue and dry it prior to examination under the microscope.
6) Upon any positive indication of crystals being present, wash the residue in fuming hydrofluoric acid in a platinum crucible.
7) Test any crystals which still persist for:

a) Chemical composition (carbon determination)

b) X-Ray diffraction

c) Specific gravity

d) Refractive index

e) Crystal habit

f) Physical tests (hardness)

CHAPTER V

Experimental Procedure and Results

Alloy Preparation

Preparation of the lead-calcium alloy was attempted by several methods. The first attempt was to heat pure calcium and lead metals in the tube furnace at 1350 K. No mixing seemed to occur. This might have been due to the high surface tension characteristic of the metals or oxide coatings on the metal surfaces.

The next method tested was to heat lead, calcium carbide and calcium chloride in a reducing environment at 1275 K (Yokoyoma et al. 1952). Four grams of calcium carbide, 10 grams of lead and 1 gram of calcium chloride were placed in a graphite boat. Carbon lampblack was used to maintain the reducing environment. The calcium chloride was used to promote dissociation of the calcium carbide. A graphite lid was used to cover the boat.

It was found necessary to pre-dry the chloride to 590 K and install drying tubes in the gas lines to prevent reaction of moisture with the carbide. The contents were placed in a graphite boat in the furnace under an atmosphere of argon. Originally, ceramic boats were used as well as nitrogen gas. The chloride was found to react with the ceramic crucible. In addition, nitrogen was first used and was replaced by argon because of the possibility of the carbide reacting to form calcium cyanamide (Richarson et al. 1940). This reaction has been shown to promote rapid graphitization of the dissociated carbide ions (Boehm, 1978).

The mixture was heated under argon for varying time durations from 2 to 24 hours. At the onset of heating, a foul smelling vapor was emitted from the tube outlet. A black film was deposited on the inner wall of the quartz only at the point where it stuck out of the furnace. The resulting film could be burned off later and it was concluded to form from the impurities present in the carbide.

Analysis of the resulting alloy (Galbraith Labs) showed calcium contents ranging from 1 to 3 weight percent and a carbon content of no more than 0.02 weight percent. The calcium content was found to increase with increasing temperature and longer heating times. Graphite, carbon lampblack or charcoal were also added in the hope of increasing the amount of carbon dissolved in the alloy. No increase was found to occur.

It was desired to increase the carbon content in the alloy to promote a higher level of carbon supersaturation during the steam treatment. This was attempted by increasing the calcium content in hope that carbon might be accepted more readily due to the increased presence of calcium. Calcium carbide was added directly to the lead (no flux was used) and heated for two hours under argon at 1425 K. The resulting product was found to contain 5 percent calcium when the reactants were added in a 2.5 to 1 ratio of lead to carbide. The newly-formed alloy was found to be significantly harder than pure lead, extremely brittle and possessed a glittering, metallic appearance.

These results were unexpected when compared to methods reported in the literature (Yokoyoma et al. 1951; Nashelskii, 1958; Aravamuthan et al. 1965 and others) where the need for a flux was deemed necessary. However, one group of workers (Hirano et al. 1979) have reported that a small percentage of calcium carbide does dissociate under argon at temperatures as low as 1275 K (the product being calcium and graphite). It was thought that impurities present in the calcium carbide might have been the source of calcium transfered to the lead. Analysis of the calcium carbide showed only calcium oxide and calcium sulfide as alternative calcium sources. These compounds maintain very high melting points and would be unlikely to react under the conditions used.

The carbon content was determined to be approximately 0.05 to 0.06 percent when the alloy was prepared with only lead and the carbide. Additional lead was then added to the alloy in an attempt to lower the calcium content to one percent. This was done because the melting point of the alloy had to be maintained below the temperatures which Burton used during steam treatments (an alloy containing 5 percent calcium has a melting point of approximately 900 K whereas an alloy containing 1 percent calcium has a melting point of approximately 700 K). The additional lead was accepted by the alloy only under agitation. This was accomplished by the introduction of a stainless steel tube into the reaction vessel with argon flowing through.

The resulting alloy was then meticulously cleaned by removing any residue adhering to its surface. The alloy was first washed in water to remove any unreacted calcium carbide. The outer surface was then removed with an iron file until only a shiny alloy remained. The alloy was then washed thoroughly in ethyl alcohol. This step was very important to insure that no graphite nuclei were present in the subsequent "diamond-making" step.

A problem encountered during the above procedure was the continual chemical attack on the quartz tube. Oxides of lead and calcium had an extremely corrosive effect on the tube. The tube would eventually crack after several runs because the oxide layer on the tube expanded or contracting at a different rate than the quartz.

Steam Treatment

The final one-percent calcium-in-lead alloy was next subjected to steam for the purpose of calcium removal. This was accomplished by passing argon, saturated with steam, over the sample at various flowrates between 80 ml/sec and 5 ml/sec. Steam treatments were tried for several time durations ranging from 10 minutes to one hour. Reaction temperatures were tried at 25 degree intervals between 775 K to 1025 K to be in the range of Burton's procedure (i.e., "a dull red heat"). The steam flow was stopped and the vessel cooled under argon. The quartz tube was removed from the furnace so that the reaction boat was exposed to room temperature. This ensured rapid cooling. Cooling times were approximately 10 degrees per minute.

Upon removal of the boat from the oven, the product was covered with a white, flakey film in addition to a smaller amount of a grey film. The white crust was identified as calcium hydroxide and the grey film was lead oxide.

Treatment of Residue

Upon completion of the steam treatment the product was allowed to cool and then dissolved in a beaker containing hot nitric acid and water in a 1 to 2 ratio, respectively. This mixture was found to be more effective in dissolving the lead than concentrated, dilute, or cold acid-water solutions. Lead nitrate crystals formed immediately. The residue was then decanted and washed several times with distilled water to dissolve the water-soluble lead nitrate and calcium nitrate from the residue.

This procedure was continued until the decanted wash was free of lead nitrate. This was determined by the addition of thioacetamide to the wash, which formed a black precipitate if lead was still present. The residue was collected by centrifugation from the remaining liquid and then dried.

The removal of other possible crystal products was important. Possible contaminants from the alloy dissolved in nitric acid were lead nitrate, lead oxide, calcium nitrate and calcium oxide. The first three of these all exibit colorless, cubic crystal structures similar to that of diamond (Weast, 1972). The lead oxide is of a tetraedral shape. As mentioned above, both lead nitrate and calcium nitrate are extremely soluble in water, the latter being three times as soluble. The oxides of lead and calcium are both soluble in nitric acid.

Attempts were made to remove graphite from the residue to isolate any diamond crystals which might have been present. This was done by the addition of tetra-bromoethane which has a density (2.96) between that of graphite (2.25) and diamond (3.51). The liquid was added to the dried residue and centrifuged. The graphite was then removed from the top of the liquid. This procedure was difficult (and not very effective) because of graphite's tendency to stick to the walls of the glass test tube.

The residue was next examined under an ordinary stereo microscope to determine if any crystalline products were present. Some graphite was usually present and appeared microscopically as a dark, opaque mass. If there was any indication of the presence of crystals, the sample was then further treated with fuming hydrofluoric acid in a platinum crucible. Hydrofluoric acid is effective in dissolving many materials, including silicates, which could have been acquired in the quartz furnace tube. Carbon is one of the few materials not attacked by the acid. The solvent was allowed to vaporize, leaving behind the remaining residue. The product was again washed with distilled water and allowed to dry. The residue was then examined under the microscope for possible crystalline products.

CHAPTER VI

Analytic Procedures and Results

Electron Microprobe Analysis

A quantitative determination of the lead-calcium alloy was performed using an electron microprobe technique. This analysis was used: (a) to compare the composition of the complexes formed in the alloy to those reported in the literature, (b) to examine the effect of steam treatment, and (c) to provide a better understanding of how carbon might be incorporated in the alloy.

Sample preparation of the alloy was tedious because of its softness. Care had to be taken to provide the finely polished surface that is essential for the microprobe technique. The sample, a cross-sectional slice of the alloy, was mounted in an epoxy resin for ease of handling. Polishing was done on successive grades of fixed diamond polishing wheels using a saturated solution of paraffin in kerosene to minimize distortion of the surface from abrasive particles (Bassett et al. 1932). Etching was necessary to remove distortions on the surface incurred from polishing. A solution of one part nitric acid in four parts alcohol was used as the etchant (Vilella et al. 1927). Successive cycles of etching and fine-polishing on a felt wheel were performed.

Figure 5 shows the polished alloy surface under a polarizing microscope at a magnification of 40 X. Two phases were evident. The lighter phase was later confirmed as a $CaPb_3$ complex in a dendritic form. The darker, continuous phase was determined to be virtually pure lead.

The microprobe analysis was performed on two samples. The first sample was an alloy prepared by mixing lead and calcium carbide under argon at approximately 1375 K. The second sample was the same alloy after steam treatment. Standards used were lead sulfide (PbS) and calcium metasilicate ($CaSiO_3$).

Sample one was shown to consist of two phases, as reported above. The discontinuous phase was found to consist of 77.2 atomic percent lead and 22.8 percent calcium. This corresponds to an approximately three to one atomic ratio of lead to calcium. This agrees well with the literature (Aravamuthan et al. 1965) where $CaPb_3$ is the expected phase. The slight excess of lead was concluded to be due to the smearing of phases normally encountered in the polishing of soft metals and alloys (Solberg, 1984). The continuous phase contained 99.6 atomic percent lead and 0.40 percent calcium. Thus the second phase was virtually pure lead as expected.

Sample two (after steam treatment) was analyzed and virtually no calcium was detected. Figures 6 and 7 show

FIGURE 5.

The Two Phases of the Lead-Calcium Alloy

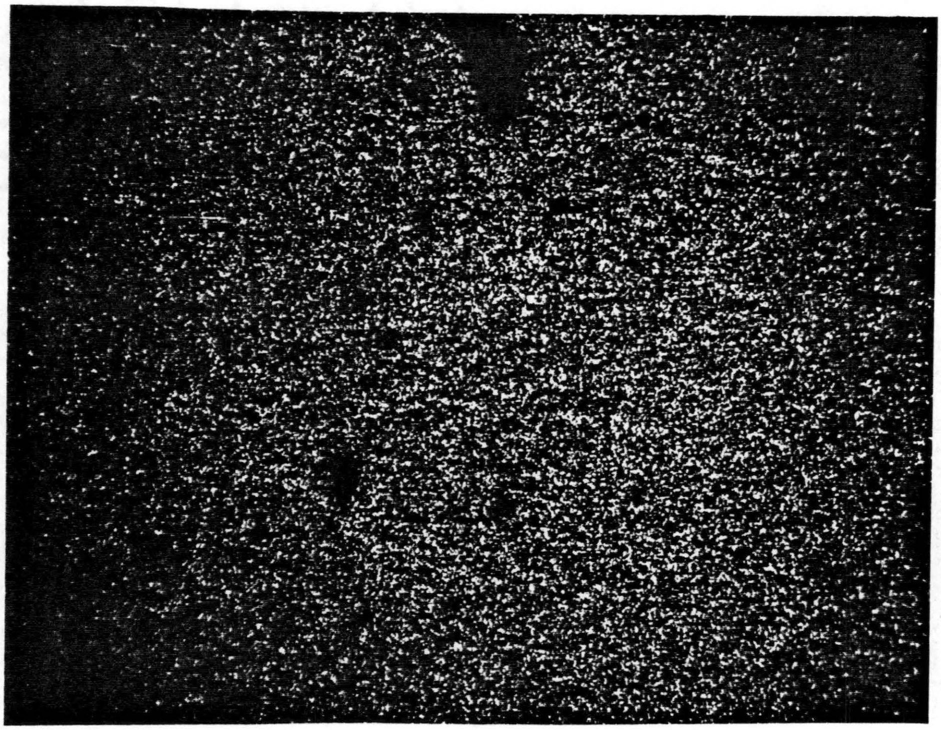

FIGURE 6.

Microprobe Photograph of Calcium Presence (bright spots) Before Steam Treatment.

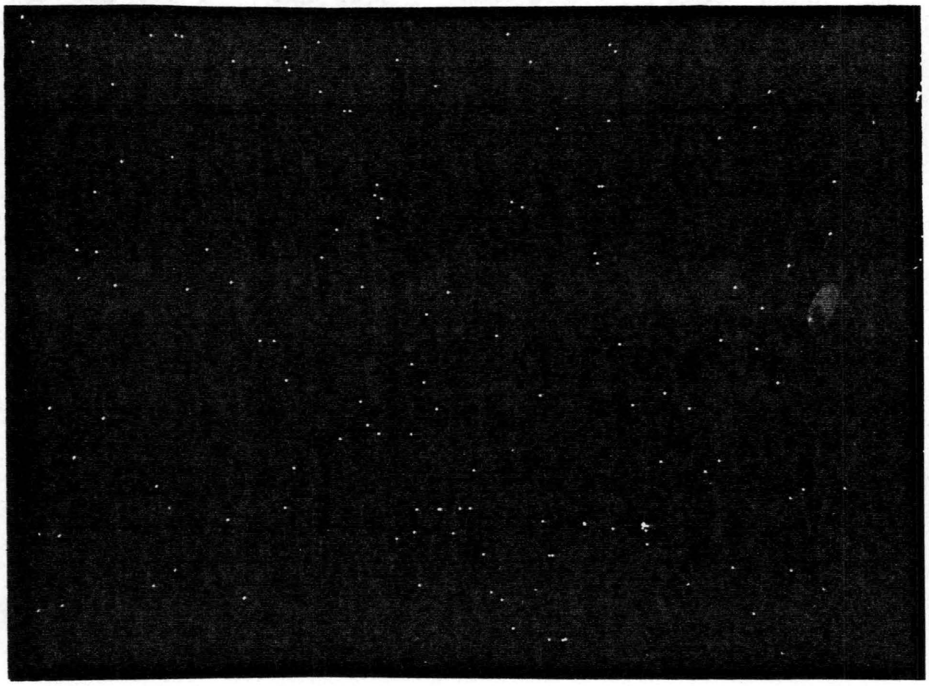

FIGURE 7.

Microprobe Photograph of Calcium Presence (bright spots) After Steam Treatment.

exposures for calcium in samples one and two (before and after steam treatment, respectively). The bright spots correspond to the presence of calcium. Small amounts of impurities were detected in the second sample. Most of these impurities contained aluminum and this was attributed to the fine alumina grit used in the final polishing step of sample preparation.

The microprobe analysis confirmed the alloy composition and the effectiveness of calcium removal by steam. An analysis of carbon in the alloy was tried but proved unsuccessful because of the relatively small amounts present and the chance of impurities to be incorporated into the sample. This was disappointing considering that no imformation is available concerning the form in which carbon may be dissolved in the lead alloy.

Crystallographic Tests For Diamond Determination

During the course of the investigation, crystals were periodically found which appeared to be cubic in form and resisted attack by hydrofluoric acid. The next tests that were used to determine if diamond crystals were present was to measure crystal angles, index of refraction, and to determine whether or not the crystals were isotropic. All were done with the use of a polarizing microscope provided by Dr. Bloss of the Geology Department at VPI.

Diamond crystals are typically isotropic (being part of the isometric class) although they sometimes show double refraction along the octahedral edges (Orlov, 1977). To determine the isotropy of any residual crystals, the sample was placed in a polarizing microscope and rotated 360 degrees under a shaded light source. An isotropic crystal reflects the light evenly in all directions. Anisotropic crystals reflect a light source more strongly along certain planes.

Because of diamond's sometimes anisotropic appearance, the index of refraction was also determined. Diamond crystals possess an unusually high refractive index of 2.417 (Weast, 1972). The measurements were made using an oblique illumination method (Bloss, 1961) by comparison with various oils of known refractive indices. A crystal was placed on a glass slide and a drop of oil with a known refractive index was placed on top along with a cover slip. The sample was then placed in the polarizing microscope. A shadow was advanced toward the crystal by gradually blocking out the light source with an opaque stop. This resulted in a shadow on the crystal. If the crystal shadow was on the side of the approaching shadow (i.e., shadow meets shadow), then the crystal has a higher index of refraction than the oil. If the crystal shadow forms on the opposite side, the crystal has a lower index of refraction than the oil.

The above method was found to be ineffective for darker crystals as shadows were difficult discern. A second method used for refractive index determinations was the Becke Line Method (Bloss, 1961). Here, the grain is viewed slightly above the point of sharpest focus. At this point, both a bright and dark line can be seen concentric with the outer edge of the grain. As the microscope is racked slowly upward, the brighter line moves toward the medium of higher refractive index. The use of successive grades of oil allowed the refractive index to be measured within ± 0.10. Examination of many residues consistently showed a refractive index of approximately 1.70. The index of refraction for graphite has been reported as 1.80 (Reynolds, 1968).

X-Ray Analysis

X-Ray analysis was performed on a limited number of samples. This method was important because of its ability to identify small amounts of crystals that might have been present in the bulk of the residue. The analysis was performed with a Philips photographic wide-angle diffraction camera (model # PW 1720). The procedure was done with the help of Dinesh Tyagi of the Chemical Engineering Department at VPI.

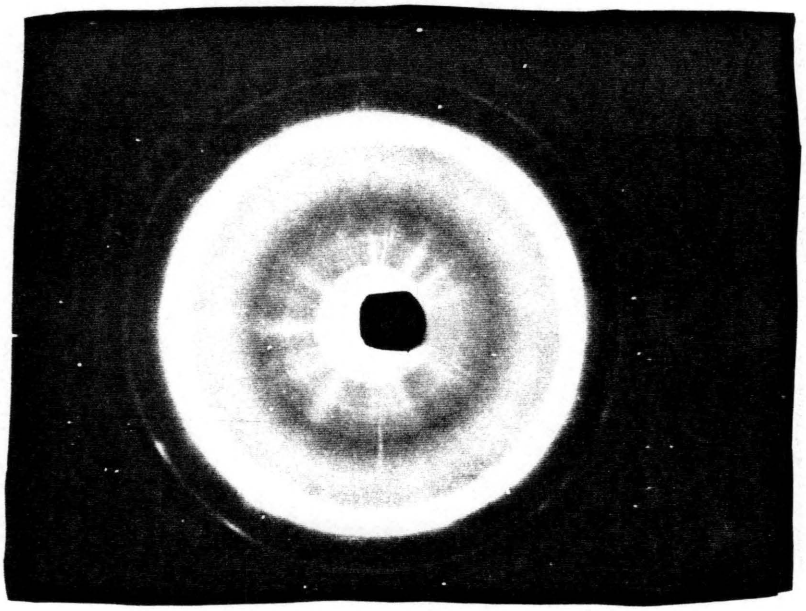

FIGURE 8.

X-Ray Diffraction Pattern of Residue

The results of the analysis are shown in Figure 8 (a representative diffraction pattern). Calculated d-spacings of the more-intense rings were 3.43 and 2.04 angstroms and these correspond to those of graphite (JCPDS, 1967). No diffraction patterns typical of diamond were found. The sharp rings present in the figure were evidence of a well-crystallized structure.

Specific Gravity Measurements

Measurement of the specific gravity of residues was accomplished by the use of a float-sink method (Bloss, 1961). The residue was finely ground and placed in a test tube filled with diiodomethane (specific gravity = 3.325 at 293 K). All particles obtained from experiments floated in this liquid, indicating that no diamond was present. Next, 1-chloronapthalene (specific gravity = 1.194 at 293 K) was added to the test tube until a mixture was finally obtained where the particles just sank after centrifugation (i.e., the density of the particles was approximately equal to the density of the mixture). The refractive index of the mixture was then measured with a refractometer. Figure 9 (Bloss, 1961) shows a correlation of the liquid's refractive index versus its density at various temperatures.

The experimental specific gravities obtained in this

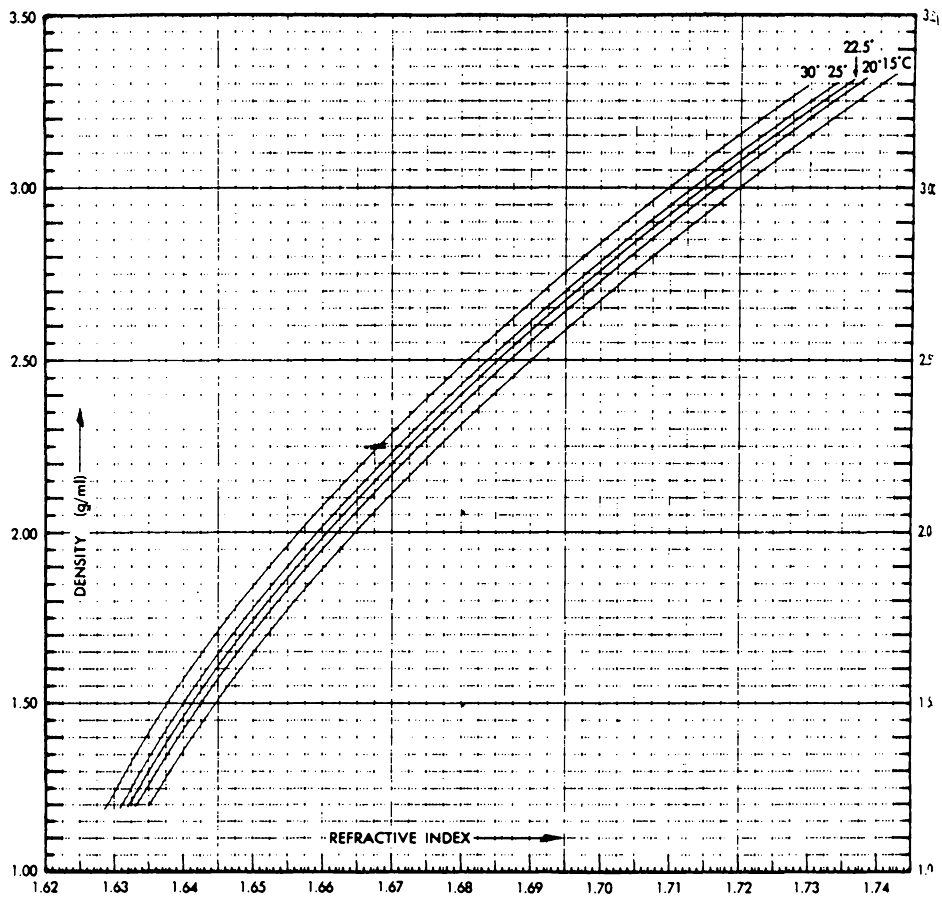

FIGURE 9.

Relation Between the Refractive Index and Density for Mixtures of Diiodomethane and 1-Monochloronapthalene fashion were consistently in the range of 2.20 to 2.25, with an experimental error of ± 0.10. The specific gravity of pure graphite at 293 K is 2.25 (Weast, 1972). In addition, a very small portion of the residue maintained a density lower than the bulk and this was thought to result from a small amount of amorphous carbon being present.

Carbon Determination

Quantitative analysis of the carbon present in the residue was performed by both Galbraith Laboratories,Inc. of Knoxville, Tennessee, and at VPI. Galbraith Lab used a coulometric method for carbon analysis which consisted of oxidation of the residue to carbon dioxide and the subsequent conversion of the vapor to ethanolamine. This liquid was then titrated to determine the carbon content of the original sample.

Carbon determinations were also performed with the use of a thermogravimetric analyzer. Here, the sample was heated in an inert helium atmosphere to 1175 K. At this temperature oxygen was introduced into the sample chamber and the weight loss recorded. The percentage carbon in the sample is then the loss in weight of the sample at 1175 K divided by the total weight of the original sample. Carbon determinations of various samples showed total carbon contents in the residue to range from 94 to 97 percent.

CHAPTER VII

Discussion of Results

Summary of Analytical Results

The final residue obtained by removal of calcium from the alloy was analyzed by both chemical and physical methods described earlier. These included:

1) solubility in various reagents
2) total carbon analysis
3) density measurements
4) refractive index measurements
5) X-Ray diffraction

The specific gravity of the precipitate was consistently found to be in the range of 2.20 to 2.25 (diamond has a value of 3.41). The refractive index was found to range from 1.65 to 1.75 (diamond has a value of 2.42). The residue was inert to chemical reagents, including hydrofluoric acid, nitric acid, hydrochloric acid, acetone and potassium hydroxide. Total carbon content of various samples ranged from 94 to 97 percent carbon. X-Ray diffraction showed sharp patterns from crystal lattice spacings typical of graphite. On this basis, the residue was determined as graphite.

<u>Carbon Solubility in the Lead-Calcium Alloy</u>

Of particular interest in this work was the determination of the solubility of carbon in lead. The amount of carbon that dissolved in pure lead was, as expected, exceedingly low. Experiments were conducted to determine the carbon solubility in pure lead. Carbon (as graphite or lampblack) was heated with lead at 1425 K with stirring. A carbon analysis of the final product was not possible because the amount present was less than 0.001 weight percent (the lowest measurable quantity of carbon was 0.001 percent for the analytical method used). It is thought that the values of the solubility of carbon in lead reported by Ruff and Bergdahl (1919) and Brinkman et al. (1964) are somewhat high. However, the results obtained are in accordance with that of Strong (1963).

The solubility of carbon in lead was found to increase as more calcium was added to the lead. Alloys of greater than 5 weight percent calcium were unable to be obtained due to the limitations of the equipment (i.e., temperature). The use of a lead-calcium alloy was found effective in increasing the amount of dissolved carbon.

The weight of residue found to precipitate from the melt correlated well with the amount of carbon initially present in the alloy. Typical yields were 3 to 4 milligrams of precipitate for 12 grams of an alloy containing 0.05

percent carbon (i.e., 6 milligrams of carbon). It should be noted that the alloy was thoroughly cleaned before being subjected to the steam.

Discussion of Burton's Method

It has been stressed throughout this report that Burton's original communication was vague in providing specific details of the experimental method. As a result, several variations of the procedure were tried. Variables in the experiment included:

1) The amount of carbon present in the alloy
2) The temperature of the steam treatment
3) Flow rate of the steam (i.e. partial pressure)
4) Time duration of steam treatment

In his original paper, Burton stated that "a molten alloy of lead with about one percent calcium appears to be capable of holding in solution some small proportion of carbon,...". In the present work, the amount of carbon introduced to the alloy varied from 0.01 percent to 0.06 percent by using alloys of different calcium content. Additional lead was then added to maintain Burton's one-percent calcium-in-lead alloy (to keep the melting point below the steam treatment temperature). No detectable amount of residue was found to precipitate below 0.02

percent carbon in the sample. Above this value, it was found that the weight of residue collected had increased.

The temperature at which steam was passed over the sample was given by Burton as "somewhere between 550 C and 700 C, or not far outside these limits...if the reaction has occurred at a full read heat, graphite is found in the crust of the lime." The reaction temperatures tried in the present experiment ranged from 775 K to 1025 K at 25 degree intervals.

Also studied was the effect of the flow rate of steam and time duration of steam treatment during the "diamond-making" step. The rate of precipitation of carbon from the melt must be proportional to the rate at which calcium is removed by steam. Other workers have shown that too high a supersaturation of carbon atoms can induce graphite crystallization because of too large a driving force for graphite nucleation (Brinkman et al. 1964). On the other hand, too low a level (below that corresponding to diamond saturation) will also produce the more-stable graphite product. In light of this, experiments were tried at various flow rates between 80 ml/sec and 5 ml/sec.

The fact that graphite was produced at reaction temperatures of 775 K strongly indicates that the carbon was incorporated into the alloy as aromatically-bound, graphitic units that are similar to the sp(2) bonding in graphite. These same speculations were made by others (NSF, 1982) to explain the failure of lead to promote diamond formation at diamond-stable pressures. At such low temperatures as 775 K, it is unlikely that free carbon, falling out of solution from the melt, can crystallize to such a well-defined graphite structure as was confirmed by X-Ray analysis. As stated earlier, carbon of a higher free energy than that of diamond or graphite would find it hard to get beyond the metastable diamond state at such low temperatures. In addition, Mantell (1968) has reported that other forms of carbon, such as carbon black, need to be heated to much higher temperatures (approximately 1575 K) to convert to the graphitic structure.

The point raised above would be better understood after future studies of the bonding character of carbon in lead and other similar metals. Most of the previous work in this area has been directed at diamond-stable pressures because of the commercial importance of such conditions. The work of Brinkman et al. (1964) has shown that metastable diamond growth of carbon from a lead solvent can be achieved from a lead solvent at temperatures of 1475 K and atmospheric pressure by epitaxial growth on the surface of a diamond seed. These results provide support for the existence of carbon being dissolved in the lead in a higher free energy state than that associated with a diamond phase. The seed crystal used by Brinkman altered the kinetics of the system. In the present experiment, graphite nucleation appears to be the preferred transformation process despite the low temperatures used.

Burton's Claim

In his letter, Burton devoted a good deal of effort to describe the properties of the small crystals obtained from his experiments. Assuming that Burton's description was honest, the properties reported were very similar to that of diamond. The crystal structure was that typical of diamond. The refractive index (found by a method similar to the Becke Line Method described earlier and used in this experiment) and chemical inertness are also typical of diamond. Burton reported that the crystals were perfectly transparent and flawless. If this method did indeed work, the slow growth rate inherent in the procedure might be sufficient to form such faultless crystals.

In the present experiment, crystals were periodically found that gave a scare of success to the author. It was difficult to conduct physical property measurements on one crystal. Silicates and lead nitrate crystals were detected in some residues along with other, unidentifiable crystals. Burton stated that his crystals were inert to fused alkali, ordinary acids and hydrofluoric acid. These reagents would attack the species mentioned above. He also stated that the crystals burned away without leaving any residue. This is a strong indication that only carbon was present.

It should be emphasized that many of the earlier claims of diamond synthesis were correct according to the analytical methods available at the time. The lack of X-Ray analysis and other conclusive identification techniques could have been the cause of a mistaken claim.

SUMMARY AND CONCLUSION

Burton's procedure for metastable diamond synthesis was investigated. The procedure involved the dissolving of carbon in a lead-calcium alloy above the equilibrium value for that of pure lead. The amount of carbon dissolved in the alloy was found to be significantly greater than the solubility of carbon in pure lead. This was attributed to the presence of the calcium.

The calcium was removed from the alloy by oxidation with steam at various temperatures between 773 K and 1023 K. The method was found effective in removing the calcium from the lead as calcium hydroxide. As a result of the calcium removal, carbon precipitated from the melt because of its presence in above-equilibrium amounts. The carbon was found to crystallize to graphite. No diamond crystals were observed in the final product.

It was concluded from these results that graphite nucleation was the dominant transformation process. A metastable state of diamond was not observed. It was hoped that the oxidizing atmosphere created by the steam would preferentially attack the forming graphite nuclei.

Burton had claimed that a metastable diamond product was formed. The properties reported in his paper were characteristic of diamond. His claim, as so many others around that time, still remains unconfirmed. The use of a diamond seed has proved to be necessary for diamond synthesis at metastable conditions. The analytical methods available in 1905 were less than adequate for positive chemical identification and this may have been the cause of Burton's mistaken claim.

In all fairness to Dr. Burton, the task of finding one small crystal in the final product was difficult (i.e., finding a needle in a haystack). The results of the present experiment do not confirm Burton's claim.

Future work in this area is encouraged. A careful monitoring of supersaturation conditions as well as the bonding character of carbon in a lead-calcium alloy can determine the feasibility of Burton's procedure. A more efficient removal of graphite during steam treatment is necessary. There is also the possibility for use of this approach for diamond synthesis on the surface of seed crystals.

APPENDIX A

A Reproduction of Burton's Article

"Artificial Diamonds"

"Nature" (London), 72 (1869), 397, 1905

Artificial Diamonds

by C.V. Burton

Of the two phases, diamond and graphite, diamond is the denser, and has also the less internal energy. It follows that, if diamond can be crystallised at comparatively low temperatures, the minimum pressure sufficing to determine the diamond form will be lower than that employed in M. Moissan's experiment.

For estimating the transformation temperature corresponding to low pressures, the data available are incomplete; it is here suggested, however, as a tentative result from experiments which are still in the experimental stage, that the transformation temperature corresponding to atmospheric pressure lies somewhere between 550°C and 700°C, or not far outside these limits, temperatures having so far been judged only by eye.

A molten alloy of lead with about 1 per cent calcium appears to be capable of holding in solution some small proportion of carbon, which exists as free carbon or as calcium carbide; and if the calcium is eliminated from the molten mass, some carbon crystallizes out. Steam, for example, converts the calcium into hydrate without attacking the lead. If the reaction has occurred at a full red heat, graphite is found in the crust of the lime; if only a very low red heat has been obtained, no graphite is found, but a number of very small or microscopic crystals, which have many of the properties of the diamond. The illustration is from a pencil drawing of a very minute crystal, viewed under magnification of 80 diameters, and drawn on a greatly enlarged scale.

The crystals obtained exibit mostly faces of the octahedron, modified by the cube and the dodecahedron; in no case has any internal flaw or lack of perfect transparency been detected in them. The refractive index is clearly very high, and an attempt to determine it by displacement of focus gave 2.43 (instead of 2.47), any convexity of the refractory surface tending to give too low a value. The crystalline faces are, in fact, generally, if not always convex, in many cases strongly so. The crystals adhere tenaciously to clean, dry glass; they are unacted upon by ordinary acids (hot or cold), by cold hydrofluoric acid, and by fused alkali at a red heat. When strongly treated on platinum foil, they burn away, leaving no residue. The quantities at present available are too small for the ready determination of density or hardness.

Negative results were invariably obtained in control experiments on the commercial calcium carbide which was used in preparing the alloys.

Tin may be used in place of lead, but it is freely oxidized by the steam, and the resulting oxide is troublesome to get rid of. Of other reactions which appear to have yielded minute crystals of diamond, the following may be mentioned: ---boiling benzene or toluene in contact with finely powered potassium dichromate or with concentrated aqueous solution of gold chloride; heating benzene or toluene mixed with carbon tetrachloride or chloroform to 200°C to 300°C in a bomb. In the last named reactions, nearly all the carbon separates out in the amorphous form, hydrochloric acid collecting under enormous pressure.

I hope shortly to return to the subject of these experiments, and to make a fitting acknowledgment of my indebtness to Mr. W. J. Hartley and Messrs. Neville and Heycock, and to other friends.

C. V. Burton

4 Chesterton Hall Cresent, Cambridge, August 19.

APPENDIX B

A Biography of C.V. Burton

by Neal Sugarman

A BIOGRAPHY OF BURTON

Dr. C.V. Burton was a man of diversified interests. He held a Doctor of Science degree from London University as early as 1893. He was both a theoretical and experimental physicist. He appears to have been a regular and extremely vocal member of the Physical Society of London and the British Association between the years 1890 and 1910. In all, over twenty publications of Burton's have been found.

Burton's favorite subject, by far, was the Ether. This was an infinitely elastic and massless medium which was presumed by many scientists, at that time, to propogate all electromagnetic waves in the universe. This was, of course, before the confirmation and acceptance of the Michelson-Morley experiments. He presented a number of papers to the British Association on this subject concerning everything from "The Sun's Motion With Respect to the Ether" to "The Ether and Electrons".

Other interests of Burton's included gravitation, astronomy, conductivity in metals and osmotic pressure. It is rather surprising that such a man would venture into the field of experimental Chemistry.

A possible answer to this question was the company that Burton kept. In the "Artificial Diamond" communication, Burton extended thanks to C.T. Heycock and F.H. Neville.

Both of these gentleman were members of the highly regarded Fellows of the Royal Society (FRS). Both Heycock and Neville were metallurgists. Their experience most probably inspired Burton to use a lead-calcium alloy.

The third person acknowledged by Burton was W.J. Hartley. Hartley appears to have been a very prominent chemist. He and Burton worked together in later years along with The Earl of Berkeley (another FRS) on osmotic pressure measurements. Thus Burton's imaginative mind along with the metallurgical and chemical backgrounds of his friends most probably set the scene for the synthetic diamond paper. It is still a mystery why any of his friends were not co-authors instead of acknowlegements.

Burton's synthetic diamond paper appears to have been the only experimental chemistry work done by him prior to 1910. His publications at this point in his career indicate a strong turn to experimental work. In 1910, he and The Earl of Berkeley published a paper (Berkeley and Burton, 1910) on bimetallic thermostats that appears to predate any other attempts on such a subject. In 1910 and again in 1920, the same two men, along with Hartley, presented extensive and thorough papers (Berkeley et al. 1910 and 1920) concerning osmotic pressure measurements of sugars and organic materials. Burton even presented a paper to the British Association recommending the use of front wheel drive to control the problem of "Side-Slip in Motor Cars" (Burton, 1904). Also of interest was a paper by D.C. Pack in 1960 on the breakdown of a continuum in a compressible fluid. In this paper, Pack credits Burton with being the first to recognize and qualitatively model the phenomena (Burton, 1893) and also states that no other workers in the field were aware of this: a remarkably similar case to Burton's synthetic diamonds.

The mystery of Burton's "Artificial Diamonds" may never be solved. No retractions, further communications or rebuttals from other scientists have been found. He was apparently an avid member of the science community and held good company. Some of his work show thoughts ahead of his time. Although some of his conceptions in the diamond article were wrong, Burton's basic idea for synthesizing diamonds in a metastable state, at that time, was ingenious.

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