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Observation and Characterization of Fullerenes in Soot Generated During Reproduction of Historical Diamond Synthesis

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ABSTRACT

Historical diamond synthesis of Henry Moissan and Dr. J. W. Hershey are recreated. By using a carbon arc furnace to melt iron samples with dissolved carbon, the molten iron was thought to trap excessive carbon in the iron lattice when it is quenched in water. This contraction was believed to compress carbon into diamond. Current research in chemical vapor deposition and thermal activation of graphite has shown that earlier diamond synthesis methods, using electric arcs, may be plausible due to the species generated in the carbon plasma of the arc. Under conditions, much lower in temperature and pressure carbon electrodes, while arcing, will generate different allotropes of carbon, including diamond. An initial experiment was run involving molten iron in an open graphite crucible under an argon blanket. Digestion of the samples from this experiment gave no visible diamond. For the subsequent experiments, an electric arc furnace was constructed making use of a V shaped electrode configuration. Experiments were run using AC and DC current, focusing on soot generation and characterization. Characterization of soot was done using Soxhlet extraction and IR spectroscopy. Soot generated from an unshielded (no argon) AC current yielded a peak match at 1384 cm^{-1} and several other overlapping regions when compared with an IR spectrum of a known sample of soot containing C_{60}. Design modifications of the electric arc furnace are proposed for further experimentation.

Keywords: *Fullerene, C_{60}, Electric Arc Furnace*

INTRODUCTION

Diamond is becoming one of the most technologically and scientifically valuable crystalline solids (Yarbrough and Messier 1990, Palnichenko et al. 1999). This is because of diamonds usefulness in machining, optics, and microelectronics. Due to the many possible functions of diamond, there have been many developments in diamond synthesis (Yarbrough and Messier 1990, Palnichenko et al. 1999). Synthetic diamonds are used commercially in grinding and drilling applications because of their hardness and durability (Yarnell 2004). Many microprocessing engineers, however, would like to use diamond, instead of silicon, for microelectronics because of its unique properties as a thermal conductor and an electronic insulator (Palchenko et al. 1999, Yarnell 2004). Diamond is one of the allotropic forms of carbon, and conventional wisdom has for many years thought that it could only be reproduced by recreating the conditions under which it forms naturally (Man Made 1966). However, within the past few years, new techniques have made diamond synthesis possible under less extreme environments (Gogtsi et al 2001, Yarbrough and Messier 1990, Palnichenko et al. 1999).

For some time now, the credit for the first reproducible manmade diamond on record has been given to a research team working for the General Electric Company (American Museum of Natural History, Man Made 1966). This credit ignores early pioneers, such as Henri Moissan and Dr. J. W. Hershey. Dr. Hershey researched diamond synthesis in the 1920's based on the work of Henri Moissan (Hershey 1928). Through research, Dr. Hershey was able to synthesize the largest diamond then on record. Dr. Hershey used carbon electrodes that heated an iron and carbon sample (Hershey 1928). The molten mixture was then quenched. The contraction of the molten iron was assumed to facilitate diamond crystal growth (Hershey 1928). This method was dismissed in the 1950's by The General Electric Company who claimed that Henri Moissan's work was unsuccessful (Man Made 1966). This dismissal was based on their research, which required pressures upward of one million pounds per square inch (Man Made 1966). In spite of this earlier claim, diamond synthesis research has now been carried out using "non-equilibrium low pressure processes" involving carbon electrodes to create diamond and other fullerenes (Hare 1999, Palnichenko et al 1999).

Of the many non-equilibrium low pressure processes, two processes are similar in that they synthesize allotropes of carbon by using carbon electrodes. One of these methods has been reported to make diamond and the other process buckminsterfullerenes. Both methods are performed under reduced pressures of Helium (Hare 1999, Palnichenko et al. 1999). The Sussex Center reports fullerene synthesis under a wide range of pressure and inert gases. The best yields are reported under reduced pressures of helium (Hare 1999). The fullerenes are synthesized with voltages and amperages similar to those in Dr. Hershey's Research (Hare 1999, Hershey, 1928).

The thermal activation of graphite shows direct diamond formation by precipitation from carbon plasma formed in a carbon arc. The diamond forms directly on substrates attached to heat sinks, but they are easily removed with hexane (Palnichenko et al 1999). This method uses amperage four times greater than those that Dr. Hershey used. (Palnichenko et al 1999, Dr. Hershey 1928). The Sussex method, used to produce fullerenes, although not as high in amperage as the diamond method, does show that other forms of carbon would have existed in the conditions of Dr. Hershey's arc furnace. There are also several reported instances in which carbon can be transformed into diamond, but these methods entail high pressures as the activating mechanism (Regueiro 1992, Erskine 1991, Banhart 1996, Job 1995). These methods describe the possibility of either using carbon cage molecules as the intermediate species or they describe an iron phase change method for diamond formation.

This lead to a conclusion that Dr. Hershey's method might have been an iron catalyzed transformation mechanism. This transformation mechanism is further bolstered by a patent for a device, which similarly to Dr. Hershey's arc furnace melted iron which contained dissolved carbon (Hershey 1928, Job 1995). Both methods also heated the mixtures for about an hour, and they were both summarily quenched. This patent, having striking similarity, gives unusually strong support for an iron catalyzed transformation mechanism. Our goal in this research is too construct an arc furnace similar to Dr. Hershey's and begin the process of exploring alternate mechanisms.

MATERIALS AND METHODS

Initial Experiment with Carbon Electrodes

Sample Prep:

Four test samples are prepared using varying types of carbon. All of the samples are mixed before transporting them to the welding laboratory. They are placed into 150 mL beakers and covered with para film.

Sample A is a control sample containing just iron. The sample weighs 58.32 g. Sample B is made of reduced corn starch to emulate Dr. Hershey's samples. The corn starch is prepared by reduction with a Bunsen burner under nitrogen. While reducing, the sample smells like burning marshmallows and turns black from its original white. The final weight of reduced corn starch added to the sample is 4.29 g, soot added, known to contain C_{60} and C_{70} fullerenes, weighs 0.01 g, and the iron weighs 58.60 g. Sample C contains 58.02 g of iron, 3.82 g of activated charcoal, and 0.01 g of the same fullerene containing soot. Sample D is a deviating sample with approximately 10 g of iron and 0.195 g of soot known to contain fullerenes.

Apparatus Set-Up:

A welding torch stand is used to support the Tungsten Inert Gas (TIG) welding torch. The electrode from the torch is removed, and the amperage is on the lowest setting to ensure no interference. The torch is supported by a D-shaped vice grip. The stand is then insulated on two fire bricks. The crucible is then placed on the torch stand. The torch stand could be grounded for different electrode combinations. The electrodes are connected to the ground and the electrode holder of a Shielded Metal Arc Welder (SMAW or Stick Welder). The electrodes are 5/16" x 12" National Carbon Company Union Carbide spectroscopic grade graphite electrodes.

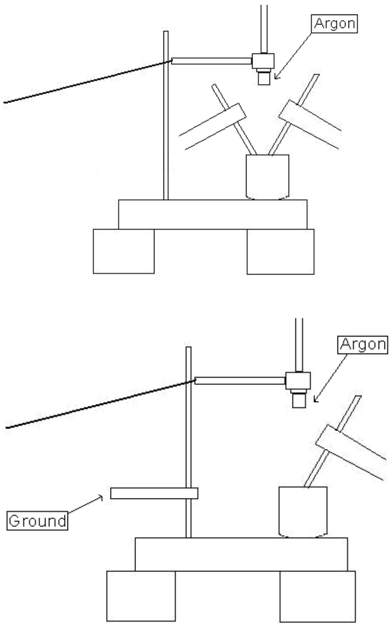

Fig 1, 2. Simple diagrams of apparatus set up.

Apparatus Testing:

Three carbon crucibles are wiped clean with paper towels until the inside is black and shiny. The welder is set at 150 A, and a crucible is used to see what electrode configuration will work inside an arc furnace. Three configurations are possible: the first includes, using the crucible as a flow from one electrode into and out of the crucible into the other electrode, second, using the crucible as a ground, and third, using a simple V shape configuration, which is finally chosen. When the electrical arc is struck between the electrodes and as the electrodes are moved closer and further away a distinctive pitch is heard.

After testing these configurations, sample A is poured inside the same crucible. An arc is then struck between electrodes, but the arc does not melt the iron sample. A DC- current of 110 A is then tried, which successfully melts the iron. The sample A is then kept molten for several minutes as all of the configurations are again tested. All of the configurations melt the sample, but the V shape configuration works the best. The molten sample A is then poured into an ice bath to quench. The sample is extracted from the bath and placed in the original container and recovered. Sample B is placed into the same crucible, but the other two samples are run using their own crucible. Samples C and D are heated for approximately two to three minutes apiece using similar rearrangements of the electrodes and then quenched. All of the samples are extracted separately and placed in the original beaker. The only deviation is that sample D, which contains only fullerene containing soot and iron, was melted with a DC+ current of 110 A.

Acid Digestion:

Each of the four samples is placed into a 1000 mL beaker. Concentrated HCl acid is added. All of the samples are then placed onto a hot plate and covered with a watch glass for digestion. Only the sample that is made of reduced corn starch had need of additional amounts of acid. As each sample is digested, the solutions progressively turn a darker green because of the iron chloride complex. The corn starch sample was the lightest shade of green and also developed a foam skin on top of the solution rather than an oily skin. All of these samples took about three weeks to digest. The solutions containing the digested samples are filtered using filter frits to collect the carbon. They are washed using deionized water. The samples are dried using an oven set at one hundred degrees Celsius. Each sample is then checked visually for diamonds, but none are found.

Furnace Design and Casting

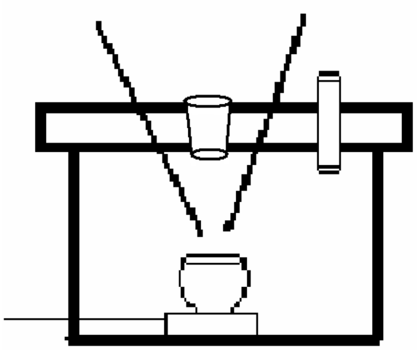

Fig. 3 Final Furnace Design

Lid Design and Initial test of Kast-O-Lite 26 LI:

Due to the initial interview with Harold Meyers and subsequent discussion with Wayne Conyers, it is most likely that Mr. Meyers' furnace was made of refractory cement. Thus, the refractory cement is needed to be tested as far the feasibility of design features. The initial design of the test piece requires that it is big enough to fit a ceramic cup (instead of TIG torch ceramic cup), a tungsten electrode, and two dowel rods to imitate the carbon electrodes. The overall dimension of width and length are then required to be 10 cm by 15 cm, and because the curing instructions are for a thickness of one inch, the thickness is decided to be 2.54 cm. A form is made of cardboard and duck tape and the inside is covered in stout plastic. A suitable amount of cast-o-lite is mixed to fill the box up to 2.54 cm. Not more than 22% water by mass is used. The block is left out until dry to the touch. After air drying, it is removed from the box along with the excess duck tape. The duck tape, should be removed or noxious fumes are released when burning. The block was then finished curing in a muffle furnace to approximately six hundred degrees Centigrade using the recommended ramp rate.

Ambient to 120 deg. Cent. @ 55deg/hr
Hold at 120 deg Cent. @ 1.5hr/in thickness
120-260deg Cent @ 55deg/hr
Hold at 260 deg Cent. @ 1.5hr/ in thickness
260 deg cent. @ 55deg/hr

It is found that the cup works well as a peep whole, when the bottom is tapped out. The tungsten electrode fits well, and can be tapped gently into or out of the furnace if part of it is broken off. The wooden dowels do not work well because the holes they make do not hold the electrodes.

Bucket Construction:

The furnace is designed around a carbon crucible that is 7.6 cm tall and the mouth is 5.5 cm in diameter. For the size of our samples, it was decided to allow the carbon electrodes to project 3.5 cm into the crucible and to allow the electrodes to arc and not have an electrode to crucible and a crucible to electrode arc. This required a minimum distance of approximately 0.5 cm.

Two cylindrical forms, one approximately 23.f cm tall by 23.5 cm in diameter and the other approximately 18 cm tall and 18 cm in diameter, are used to create the bottom of the furnace. The smaller form is elevated by 2.5 cm and centered inside of the larger form. This is followed by creating two small holes straight through both forms. The first hole is located through the side of both forms, 1cm above the bottom of the smaller form. The second hole is located directly above the first by 6.5 cm. The holes are made to facilitate the placement of two tungsten electrodes.

The form is filled by pouring a uniformly thick layer of cement to 2.5 cm, followed by the centering of the smaller form inside the larger. The holes must be aligned so the electrodes can be pushed through the holes. The cylindrical space created by the walls of the two forms is then filled with cement, and the top is smoothed out. Due to the displaced cement, the smaller form may have to be weighted.

The bucket is then allowed to air dry, followed by oven heating loosely following the recommended curing ramp rates up to about 200 degrees centigrade. Final curing is done while running the furnace, following Harold Meyer's research.

Lid of Furnace Construction:

The form for creating the lid is a wide cylindrical shape that is 22.9 cm in diameter and approximately 2.5 cm thick. The lid for the furnace uses the inside diameter of the bucket, which is 18 cm, to create the perimeter of the space that the design features are limited to. The electrodes are placed along the perimeter on opposite sides. The peep whole is located in the middle of the two electrodes, and the argon inlet is placed on the perimeter as well, only perpendicular to the line of the electrodes. The electrodes are also set at a sixty degree V shape towards the bottom of the furnace. The electrodes, crucible, and TIG welding tip are covered in duck tape and then taped to the bottom of the form. The electrodes are also placed through the form, and the tips are tapped to ensure correct geometry. The form is then filled with cement and allowed to air dry. The lid is followed by curing in an identical manner as the bucket.

When both the lid and bucket are dry, they are taken to the welding laboratory and a TIG welder is attached to the furnace, following removal of its electrode. The furnace is allowed to fill with argon providing a blanket for several minutes. A TIG welder is converted to a stick welder, and the electrode holder and ground are attached to electrodes. The furnace is then activated and allowed to cure the furnace. The bucket part, however, cracked under heat. So a suggestion by Roger Stout, a consulting technology professor, suggested using a smelting crucible. This crucible worked well for soot generation.

Soot Generation:

One of the many possible mechanisms for Dr. Hershey's method is an iron catalyzed method involving exotic precursors. This led to the proposal of soot generation and characterization. Two trials were proposed. These trials are run in the hope that a species of carbon might be identified as an exotic precursor in the Hershey method. The first run uses an argon blanket and is run with a DC- current of 175 A for about 55 min. This run produced about 4 g of dark black soot that was easily removed from the furnace. The second trial was done in a similar manner; only the furnace was run using no inert gas and a AC current of 175 A for about 55 min as well. This run produced a thin layer of approximately 2.5 g of very dark brown-red soot which was difficult to remove. In both trials the arc was not constant because it erodes away. Due to the design of the furnace, the electrodes had to be manually fed every few minutes.

Final Trial Run with Iron:

The final run was done with an argon blanket using an AC current of 175 A for approximately 55 min. This time, a crucible was placed inside of the furnace, and a thick layer of black soot developed which was removed. The iron sample did not become hot enough to quench, however, it did melt and dissolve some carbon. The iron sample was digested in HCl acid similarly to the first four iron samples.

Soxhlet Extraction:

The soot generating runs are Soxhlet extracted in attempt to concentrate any fullerenes present. Approximately 2 g of carbon soot from the DC- run are loaded into a Sohxlet thimble and covered with a plug of glass wool. The thimble is placed into the Soxhlet extraction apparatus. Toluene and a boiling chip are placed into the round bottom flask. About 3.5 g of carbon soot from the AC run are placed into a similar Soxhlet apparatus. Both extractions were left to proceed for about three hours. Both samples are put in rotational evaporators. The Soxhlet extraction done with DC- current was flooded when being rotovaped. The AC current, however, was distilled, and the residue checked for carbon. The signal from the sample was lost due to the silicone grease signal. The residue is then washed with petroleum ether to remove the silicone five times.

Characterization:

All of the samples generated except for the first trial runs were analyzed using FTIR spectroscopy and checked against a sample of soot known to contain C_{60} and C_{70}. A suspension of soot is made with 5ml of toluene and 5 ml of *o*-dichlorobenzene and is poured on a suspension of silica gel-charcoal column. The column is made by using a 10cm by 4 cm in diameter column and plugging it with glass wool, a 1 cm layer of sand, and silica gel. The valve is opened on the column and allows the solution to drain until there is no more liquid above the top of the silica bed. More of the 1:1 by volume mixture of toluene and *o*-dichlorobenzene is added until the violet band starts to elute. After the entire violet band elutes, stop the collection, and evaporate the fraction with a vacuum pump under nitrogen with a trap.

RESULTS AND DISCUSSION

Fullerene Synthesis

The initial trial samples were tested for diamond only visually. No diamonds were found in any of the samples. The soot generated from the furnace test runs were tested qualitatively with Fourier Transform In-fared (FTIR) analysis. The soot from each of the soot generating runs was tested for Fullerenes by comparison with a sample of soot known to contain C_{60} and other fullerenes. In all most of the samples matched up with a large peak at 1384 cm^{-1}, and they also matched up in several overlapping IR regions.

The Sussex Center's research shows that pressure and atmosphere inside the reaction vessel is crucial to fullerene production (Hare 1999). This and another factor, which our furnace had little control, over was arc distance control, which is crucial to other exotic carbon forms during carbon arc production (Fan). These crucial factors show that our furnace is not necessarily comparable to Dr. Hershey's design, which shows a vessel that has a close-fitting side door, and a mechanical electrode feed device. Our vessel had a poor fit between the smelting crucible lip, and our lid had little or no control over the arc.

Suggestions for Modification

Although the furnace was successful in generating soot, the design of the furnace could be readily improved upon. The furnace, itself, is difficult to open, and the crucible is more difficult to remove in a timely manner. There is no electrode arc control. The furnace would be better served by a furnace similar to Dr. Hershey's, with a side port, which would facilitate crucible extraction. One of the other major design flaws is the lack of smooth, continuous electrode feed. In order to advance the electrode, the reaction must be stopped and the electrodes advanced by hand. Another related design flaw is the imprecise placement of the electrodes due to casting. A precisely aligned gear-driven mechanism that would hold the electrodes would provide better feed control, which could also provide crude control over temperature. Feed control and the geometry of the electrodes may be central factors in this method, since carbon plasma is directly affected by them (Fan et al.).

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