

Hershey Diamond Synthesis: an Attempt at Verifying Methods

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ABSTRACT

Following the procedure for diamond synthesis, reported by J. Willard Hershey in 1929, verification of his methods were attempted in this research. A sample of soot in molten iron was generated and analyzed using Raman and Infrared spectroscopy. The soot was generated using an electric arc with carbon electrodes at 150Amps with a DC± current for 50 minutes. The iron mixture was cooled in an ice bath followed by HCl rinsing to free the iron from the mixture. Purification of the soot was done by liquid phase oxidation, air oxidation, and Soxhlet extraction. These purified and raw samples of the soot were tested and analyzed using Raman and Infrared spectroscopy. These methods of characterization showed no presence of diamond. However, the Infrared spectra showed a new product at 1090cm^{-1} , possibly representing carbon rings and ribbons. Soxhlet extraction showed an orange color, characteristic to fullerenes in solution. While this experiment showed no production of diamond, methods of characterization were established for future experiments.

Keywords: *diamond, carbon, graphite, fullerenes*

INTRODUCTION

Diamond, one of many allotropes of carbon, has many remarkable physical properties. These include having high thermal conductivity, strong covalent bonding, a cubic lattice, a high density of atoms, and extreme hardness (Angus, C.A et al., 1988). These characteristics make diamond applicable for tool coatings, corrosion protection, microelectronics (Angus, C.A et al., 1988 & Yarbrough, W.A et al., 1990), abrasives (Lou, Z et al., 2003), and lubricants (Osswald, S et al., 2006). Diamonds' versatility therefore makes synthetic diamond a popular topic among current researchers.

One of McPherson College's own, professor J. Willard Hershey, reported he and his students created the largest synthetic diamond to date in 1929 (Hershey, J.W, 1934) using simple methods based on earlier work by French scientist Mossian. A reduced sugar and iron mixture was placed just below two graphite electrodes in a carbon arc furnace. An arc flowed through the electrodes, heating the iron and melting it. Pouring this mixture in an ice bath causes a rapid temperature change, and thus a large pressure change in the iron mixture. The compression on the carbon particles is the mechanism in which Mossian and Hershey believed to produce diamond particles. Throughout five years of research it was reported that Hershey and his students produced over 50 diamonds, the largest being $2 \times 1.5 \times 1\text{mm}$ (Hershey, J.W, 1934).

However, in the mid 1950s, General Electric claimed that when they tested Mossian's methods, no diamond was formed (Bundy, F.P et al., 1955). Using high temperature, high pressure (HTHP) methods, they reported synthesis of diamond in 1954 (G.E. 1966). These claims were refuted in the late 1950s when researchers analyzed this early

experiment called "run 151 diamond." It was found that a fragment of natural diamond was mixed with the products (Bovenkerk, H et al., 1993). Analyzing G.E.'s results and methods proved that they were not good enough to synthesize diamond in that early experiment (Bovenkerk, H et al., 1993). Uncertainty in General Electric's early experiments could mean they were also wrong about Hershey's methods being unsuccessful. There is also uncertainty in whether G.E. used an electric arc furnace to reproduce the earlier work.

Today synthetic diamonds are made using various methods. The previously mentioned HTHP method is actually successful but extremely expensive. Chemical vapor deposition (CVD) (Angus, C.A et al., 1988) is widely used but methods like hydrothermal synthesis and the reduction of carbide (HSRC) (Wang, C.X et al., 2004) and thermal activation of graphite (Palnichenko, A.V et al., 1999) are successful and cheaper than HTHP. Of these, thermal and electrical activation of graphite is most similar to Hershey's methods.

Thermal and electrical activation of graphite produces hundreds of small diamonds around $10\mu\text{m}$ in size. A pulsed current is sent through pure graphite electrodes to generate an arc. High temperatures are generated and a pressure between 0.01-0.05 torr is maintained. Substrate plates of various substances sit below the electrodes by 10mm and a heat sink of copper keeps the substrate near room temperature while heat is generated above (Palnichenko, A.V). These researchers report that the diamonds are forming between the carbon electrodes where a dense carbon vapor is present; and then fall onto the substrates (Palnichenko, A.V). The similarity of thermal activation of graphite and Hershey's methods

for heating the furnace could support the reported synthesis of diamond in 1929.

The purpose of this research is to eventually verify if synthetic diamond could have been created by Hershey's methods. The methods will be followed as closely as possible with some modifications due to the ambiguity of some details and unavailability of resources. These modifications will be reported later in detail. To analyze the results of this experiment, modern spectroscopic techniques are used.

MATERIALS AND METHODS

Soot Generation

Carbon soot is generated using an arc furnace similar to Hershey's. A mixture of iron and reduced carbon in a 2:1 volume ratio, 52.4g iron to 3.2g carbon, is placed into a graphite crucible. The crucible is placed inside a larger metal forging crucible which serves as the oven chamber. Graphite electrodes of 99% purity are placed into a lid for the large crucible. These electrodes are placed so that the tips were close but not touching. The graphite crucible is adjusted in height, with a brick, so that the electrodes sit just above the iron-carbon mixture.

Using a welder as a power source the alligator clips are attached to the electrodes. The apparatus is run on a DC- current for thirty minutes at 125 amperes, tapping the electrodes down to maintain the arc as they were consumed. For another 25 minutes, the apparatus is run on a DC+ current with 125 amperes, again, tapping down the electrode as it is consumed. The arc over time is not continuous. During this process, the carbon-iron mixture turns molten red due to the high temperature created by the arc. It is assumed that a carbon dioxide atmosphere is created by oxidation of carbon. This oxygen free atmosphere was observed when the lid of the oven is taken off the oven crucible and flames are produced due to the introduction of oxygen. The molten mixture is poured into an ice cold water bath for fast cooling. However, not all of the mixture could be poured in, the portion left over is allowed to cool slowly.

Since none of the iron is consumed during the synthesis, it is removed from the mixture by dissolving it with concentrated reagent grade HCl and low heat. This process takes about three weeks. The carbon soot is collected by filtering with a fine filter frit under vacuum. 5 g of soot was collected and is in appearance, black with some shimmer. There is a mixture of matte black particles, particles with shine and what looked like sheets of carbon.

There is most likely more than one kind of amorphous carbon in the soot, mixtures of sp^2 and sp^3 carbons. To separate these amorphous forms and to isolate the sp^3 carbons, several methods were used.

Liquid Phase Oxidation of sp^2 Carbon

Approximately 1g of carbon soot is oxidized by concentrated sulfuric acid and nitric acid in a 3:1

ratio, 30ml of H_2SO_4 and 10ml HNO_3 , at $90^\circ C$ for 30 minutes. The orange liquid mixture is decanted off and the remaining carbon is filtered through fine filter paper by gravity. The amount of carbon did not seem to change drastically, but the appearance of the black soot seems to have more visible sparkle to it.

Air Oxidation of sp^2 Carbon

A second method used to purify the sample is by air oxidation (Osswald, S et al., 2006). This method uses heat to separate sp^2 from the desired sp^3 carbons. In a range of temperature between 400 and $430^\circ C$, the rate at which sp^2 carbons oxidized is far greater than the rate of the sp^3 's, limiting their loss. About 1 g of soot is oxidized for 2 hours in a muffle furnace, with a difference in mass of .044g. About half of the soot oxidized in the muffle furnace is oxidized in a tube furnace for another 3 hours, only losing .003g. A thermocouple was used to observe the temperature. It was calibrated with a melting point apparatus and known melting point compounds.

Soxhlet Extraction

Buckminsterfullerenes, another pure form of carbon, are potentially present in the soot as well. The literature reports they are produced most efficiently by electrical arcs. To help determine if they are a product of the synthesis, a Soxhlet extraction is performed with 1 g of soot. The extract is analyzed using a Fourier Transform Infrared (FTIR).

RESULTS

Several spectra were collected through Raman spectroscopy. The spectra of all samples show three common peaks at 3270cm^{-1} , 2250cm^{-1} , and 1235cm^{-1} . None of these peaks represent the characteristic peak for cubic diamond. Other observations of the spectra is that the intensities of each spectrum are extremely small, indicating that the products in the soot are not very Raman active. The peak at 3270cm^{-1} showed signs of photodecomposition with the increasing numbers of scans.

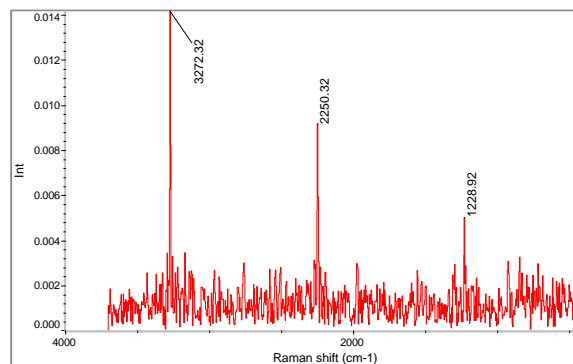


Figure 1. Raman spectra of soot after synthesis, oxidized by air in muffle furnace for 2 hours.

FTIR spectra from samples showed a different peak than the pure electrode spectrum at $\sim 1080\text{cm}^{-1}$.

Although this is not the diamond peak for IR it does show that a new product is formed during synthesis.

FTIR was also used to characterize extract from the Soxhlet extraction. No good spectrum could be taken due to the abundance of silicon oil from the stopcock grease in the sample. However, an orange color, characteristic of fullerenes in solution, was present in the solvent due to the extraction process. After evaporation of the solvent, a dark residue was present in the silicon oil.

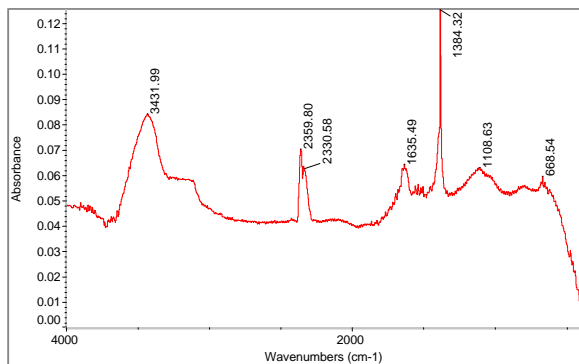


Figure 2. FTIR spectrum of pure graphite scraped from the electrodes before synthesis which serves as a blank for all other spectra of samples after synthesis.

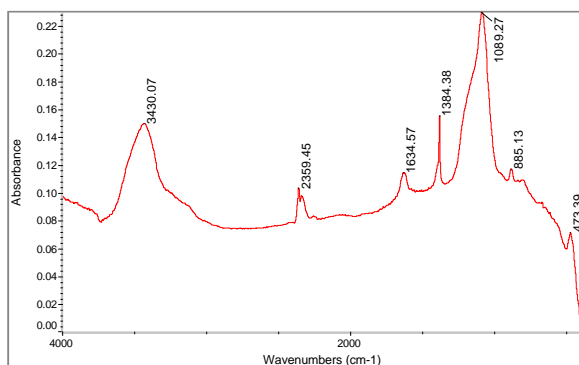


Figure 3. FTIR spectra of soot after synthesis, oxidized by air in a muffle furnace for 2 hours. A comparison with pure graphite shows a change in ratio between 3430cm^{-1} and 1384cm^{-1} and a new peak at 1089cm^{-1} .

DISCUSSION

It is obvious from the spectra of Infrared and Raman spectroscopy that there is no diamond present in the soot prepared. However, no conclusion can be made on the validity of Hershey's results because this experiment was only performed once. Many variables could be changed that may play a role in the production of diamond particles.

However, it was mentioned above that there is evidence of a new product. Infrared showed a peak present in the soot sample that was not present in graphite at 1090cm^{-1} . Reuben May, who conducted this research last year, also showed a peak at 1089cm^{-1} (May, R 2006).

Generally, in a range of $1300\text{-}600\text{cm}^{-1}$ for Raman and IR, CC alicyclics and aliphatic chains are

represented (Grasselli, J et al. 1991). The peak, 1090cm^{-1} , shows up strongly in IR. Along with this, the peak at 1231cm^{-1} in the Raman spectrum is also in this range. These peaks could correlate to the presence of carbon chains or ribbons and rings.

As mentioned earlier, fullerenes may be present in the soot, due to similar methods of synthesis. Researchers have reported peaks characteristic for the fullerenes C_{60} and C_{70} as carbon smoke. With strong IR peaks at 1429 , 1183 , 577 , and 528cm^{-1} , and weaker ones featured around 2330 and 2190cm^{-1} (Krätschmer, W et al. 1990). The strong peaks are not compatible with the peaks of the soot spectra. However, all IR readings were taken using the sample as a solid in KBr pellets, not as a vapor. *Taking a reading of the sample in this phase could give a more accurate picture for fullerene presence.* However, the peak at 2330cm^{-1} is compatible with the IR spectrum above. This is explained to be the possible attachment of CO_2 and CO to a small amount of the carbon molecules in the soot (Krätschmer, W et al. 1990).

Similar characterization of fullerenes has been done with Raman spectroscopy, showing peaks similar to the soot readings at 1232cm^{-1} , associated with C_{70} (Bethune, D et al. 1990). This one peak shows that there is a possibility of fullerene presence.

It is found that molecules with high symmetry, vibrations of the molecules can not be present in the same region of both Raman and IR spectra (Grasselli, J et al. 1991). On this note, it is to be mentioned that in the region of $2250\text{-}2100\text{cm}^{-1}$, $\text{C}=\text{C}$ is characteristic. Raman should have a peak at a very strong intensity and IR should be weak or zero, which is represented in the two spectra shown in Figures 1 and 3. There is a strong intensity at 2250cm^{-1} in the Raman and none in the IR.

Overall, there is a lot of evidence showing that a new product was formed, using the synthesis methods of Professor Hershey. Further examination should be done to classify the product created.

While no diamond was created in this experiment, it is not to say that the methods don't work. Reproducing the experiment is difficult due to lack of detailed descriptions. With further experimentation diamond could be a product of Hershey's methods.

ACKNOWLEDGEMENTS

Thanks should be made to the Technology Department and Roger Stout for allowing us to use the department welder and for all the assistance in using the equipment. I am grateful for Wichita State University in allowing us to use their Raman Spectroscopy and for Dr. Kevin Langenwalter for his assistance in using the equipment.

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