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Testing the Methods of Dr. Willard Hershey in Historic Diamond Synthesis

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ABSTRACT

The methods of Dr. J. Willard Hershey and French Chemist Henri Moissan are tested. Carbon is suspended in molten iron and cooled rapidly in an ice bath to produce temperatures and pressures suitable for diamond synthesis according to Hershey's research. A carbon arc furnace was constructed from refractory cement incased in steel pipe. The furnace is powered by an arc welder with settings of 135amps and AC current. This is run for one and one half to two hours to produce the heat required for melting the iron sample. After rapid cooling, the iron is removed with HCl. The search for diamond in the generated soot resulted in no visible examples. Raman spectroscopy was used to analyze the soot. This research has ended with no formation of diamond, but has provided techniques that will be beneficial for future research.

Keywords: *carbon, graphite, diamond, carbon arc furnace*

INTRODUCTION

Carbon, one of the most common elements in the universe, can have many uses. "It can be slippery, messy graphite worth a few pennies a pound; and, at the other extreme, it can be magnificent diamond" (Suits, C. O., 1964). For this reason, the synthesis of diamond has been the goal for many scientists of the past and present.

In 1929, on the campus of McPherson College, Dr. John Willard Hershey along with his students claimed to have produced the largest synthesized diamonds known at that time (Hershey J. W., 1940). Some even considered this the first synthesized diamond in the United Sates. The method used by Hershey was based on the work of a French chemist Henri Moissan. The procedure involved using a carbon arc to produce the heat required to dissolve carbon in molten iron, and rapid cooling to provide the required pressure. In the 1950's General Electric decided to test the methods of Moissan and were unsuccessful, dismissing both Moissan's and Hershey's work (Schulz, W., 2004). They began to work with high temperature and pressure experiments, and produced what are now considered the first man-made diamonds (Yarnell, A., 2004). They also claimed that Hershey would not have been able to synthesis diamond with the methods he reported due to the lower temperatures and pressures. Since that time much advancement has been made in the field of diamond production. To date, research is still being done to determine a way of synthesis to be both affordable and produce high quality diamond.

Today, man-made diamonds are used in abrasives, tool coating, bearing surfaces, and microelectronics (Painichenko, A. V., 1999). Many of the procedures of producing diamond use high pressure and are done at high temperatures. Because of this the costs are higher, but the product can be larger crystals. This is seen in the production of diamonds by the Gemesis Company in Florida (Yarnell, A., 2004). Using a seed diamond and high pressure over three days, a 2.8 carat rough diamond can be formed (Yarnell, A., 2004). This is progress in terms of size from what Hershey claims to have found in the 1920's. If size is not the goal and quality is, then high temperature and pressure is not the answer.

To produce a higher quality diamond, lower temperatures and pressures are required (Yarnell, A., 2004). This is what makes Hershey's experiment important. He believed that the mechanism for the synthesis was due to the compression of the iron, and because of this many methods were used to cool the iron at faster rates (Hershey, J. W., 1940). Two recent experiments have been done to test Hershey's methods, and they ended with no diamond found in the product (Hoffert, R., 2007, May, R., 2006). Two inconclusive experiments are not enough to say that it is impossible to produce diamond with these methods. Evidence of present day experiments such as the synthesis of diamond using chemical vapor deposition have been successful at lower pressures and temperatures (Wan, Y. Z., 1997).

The purpose of this research is to synthesis diamond, using John Willard Hersheys Methods from 1929. Doing this will provide evidence that Hershey was able to synthesis diamond, as he had claimed. The procedure will follow as close to the original procedure as possible, any changes will be noted throughout. This research follows two previous attempts of Reuben May (2006) and Ronda Hoffert (2007).

MATERIALS AND METHODS

Furnace Design and Construction

Hershey's Furnace: The original furnace is unable

to be located. In 1929, a furnace that could reach the temperatures required could not be found. A machinist in Chicago believed he could build one that could do what Hershey needed. He designed and constructed a carbon arc furnace that was side loading, able to move electrodes in and out of the top, and was about the size of a two gallon bucket.

Figure 1. Dr. Hershey's Furnace

My Furnace: My carbon arc furnace was designed based on the photos of the original furnace. It was constructed with a 12 inch diameter 1/8 inch thick steel case. To this legs were added and a side loading door. A solid wax mold of 8 inch diameter was placed in the middle of this outer case. Refractory cement 2 inches thick is poured around the wax mold. The brand of cement used was KAST-O-LITE 26 LI, which is able to withstand temperatures of 1425°C. Holes were left in the top where electrode holders would be attached along with bolts imbedded into the cement to hold them in place, but also making them removable. The cement was allowed to dry and the wax was melted out. Electrode holders were designed and constructed to be able to move the electrodes in and out of the furnace. This was done by welding gear rack on a moveable rod and having a small gear welded to a shaft mounted to an outer pipe. Handles were attached to this shaft. The rod can move in and out of the pipe by turning the handles. The furnace was run three times to help dry out the cement. An important design feature of the furnace is the working front door for easy removal of a crucible, while maintaining an air tight seal.

Figure 2. Furnace Constructed for My Research

Sample Preparation

Hershey's Synthesis: A number of different carbon sources were used in Hershey's experiments. Some of these included different types of sugars, starches, and one experiment used gum arabic, which was said produced a diamond. A sample of one of these materials is slowly heated using a Bunsen burner to produce the carbon needed for syntheses. A ratio of 2:1 by volume iron to carbon is added to a graphite crucible.

My Synthesis: Potato starch was used to make the carbon needed for trials 1-5. The final trial used gum arabic for its carbon source. The potato starch was placed in a ceramic crucible and a Bunsen burner was used to slowly cook the starch. This process takes about 45 minutes and a final product of black carbon was produced. Five samples of iron and carbon were prepared for trials 1-5. The ratio 2:1 by volume iron to carbon was used. This is about 52.4g iron to 3.2g carbon. Using a balance, the first 5 samples were prepared and labeled in specimen jars. The final trail using gum arabic was prepared in the same way. The ratio of 2:1 was also used in the final trail.

Soot Generation

Hershey's Synthesis: The graphite crucible containing the iron carbon mixture is placed in the furnace. The original furnace required over 10,000 watts of power and was run for one hour. During this time the arc was maintained by moving the electrodes. The crucible was then removed and the glowing white hot iron was rapidly cooled in a ice water brine. It was believed that the rapid cooling would provide the pressure needed for synthesis. After cooling, the iron was removed with a mixture of nitric and hydrochloric acids with heat. After filtering, carbon soot is left in which a diamond could be found.

Trial 1: For the first trial, the iron and carbon mixture was placed in a graphite crucible and then placed in the furnace. An arc welder set to AC current was used as the power source. The arc volt output of the welder was 25 volts, and it was set at 60 amps. The experiment was run for 1 hour 13 minutes. 5/16 x 12 inch. spectroscopic carbon rods made by the National Carbon Company were used for electrodes. The electrodes were moved in and out of the furnace to maintain the arc. During this time the furnace was steaming, due to the cement that still retained moisture from casting, making the arc harder to maintain. After the run, the iron had not completely melted, prompting a change for trial two.

Trial 2: The settings on the welder were changed while running the experiment for trial two. The settings included 12min. at 100amps, 15min. at 80amps, 10min. at 65amps, 5min. at 85amps, and 9min at 100amps. Changing the amperage during the run allowed for higher temperatures to be achieved. The furnace was opened and a flame was seen as

oxygen entered the open door. The inside was a red glow, and the iron was melted, but not hot enough to pour. Due to this, the crucible was placed back into the furnace and allowed to cool slowly. Looking at the chunk of iron under a dissecting microscope, a crystalline structure was observed on the surface. Using hydrochloric acid this piece was removed and using a muffle furnace it was tested to see if it would burn. Diamond burns at 800 degrees Celsius so the furnace was set to 1000 degrees Celsius. A platinum crucible was used for the sample and when removed the crystal was still present in the bottom. The sample was also tested with HF and was found to dissolve in its presents. This determined that the crystal was not diamond.

Trial 3: The settings for this trial included 15min. at 100amps, 25min. at 85amps, 10min. at 100amps, and 11min. at 130amps. Again in this trial, the iron became molten, but was not able to be poured. It was also allowed to cool slowly in the furnace.

Trial 4: The welder was set to 135 amps and was run for 1 hour and 29 minutes. To achieve this time, the electrodes were replace with a new set after 50 minutes. The iron in this trail was hot enough to come out of the crucible, but did so in a solid mass. I felt the furnace still needed to become hotter. Cooling was slower and more ice was recommended for the next trial. The crucible also formed large bubbles on its outside.

Trial 5: The welder was set to 135 amps and was run for 2 hours and 1 minute. Again the electrodes were replaced, but at this time at about 1 hour and 15 minutes in. During the run the outside of the furnace became hot enough to burn away the paint. The iron was melted into the crucible making it impossible to pour, due to this the crucible was dropped into the ice water, but again cooling could have been better. This time the crucible sat on the ice before lowering into the water below. Temperatures reached in this trial were great enough to melt the upper fourth of the furnace by about half an inch.

Trial 6: For the final trial the welder's settings were turned up to 145 amps and it was run for 1 hour and 35 minutes. Again the electrodes were changed after an hour. Due to the melting from the previous experiment, more heat was being lost form the top of the furnace. The iron easily poured from the crucible and the ice water bath quickly cooled the iron. Of all six trials, this one I would say was most accurate to Hershey's methods.

Removal of Iron: The masses of iron were placed in beakers of concentrated HCl to remove the iron leaving the carbon soot. The acid was change twice daily and heat was applied using a hot plate to speed up the reaction. This process is done over a 3 to 4 day period. HF was then used to remove anything else in the sample that was not carbon. This was done over a 2 day period; no heat was required for this process. The soot is finally collected by filtering under vacuum using a filter frit.

Characterization of soot

Raman Spectroscopy: Raman Spectroscopy was used to characterize the soot samples. Samples from each of the trials were tested and peaks were compared with that of known samples of diamond ($1333cm^{-1}$), graphite ($1580cm^{-1}$), and fullerenes ($1470cm^{-1}$).

Toluene Extraction: Hot toluene was used to extract the soot samples to determine a presence of fullerenes. UV-Vis was then used to analysis these extractions. A know sample containing fullerenes provided peaks at 407nm, 472nm, 548nm, and 595nm, which samples were them compared.

RESULTS

The furnace was able to reach temperatures high enough to melt the iron (1535°C) in the crucible. The exact temperatures reached for the trails are unknown, but in Trial 5 the temperatures exceeded the melting point of the cement (above 1425°C), melting the top fourth of the inside of the furnace.

The samples of carbon from trials 2 through 6 were observed under a microscope. A white unknown material was observed in the samples. To remove this unknown, the samples were digested in concentrated HF for two days. This removed the material and left only carbon behind. The carbon was then sorted through looking for traces of diamond, with nothing being found. Trial 5 showed the formation of graphite sheets and spheres along with the soot.

Raman Spectroscopy provided some evidence for the presents of graphite in all the samples of soot tested. There were no peaks associated with that of diamond or fullerenes in these samples.

Toluene extractions provided possible evidence of the presents of fullerenes in trial 5 with peaks at 464nm and 514nm.

DISCUSSION

There was no evidence of the synthesis of diamond. Exact duplication of Hershey's methods was not achieved. To be more accurate with the procedures, a power source with a greater output should be used. I believe that the temperatures required were achieved, but longer times were required due to the lower output of the arc welder.

My research did not provide evidence in favor of Hershey's methods, but did provide additional information that will be useful for further research. There are many variables, and at this time it is not sure the mechanism that will guarantee a diamond. Only six trails were completed in my research and of those I feel that only the final three came close to the original procedure. The challenge is achieving the

heat required to melt the iron-carbon mixture. Another variable is knowing what carbon source creates the diamond. More research will need to be done to definitively show that it is possible to synthesis diamond or not with these methods.

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