SYNTHESIS OF GRAPHITE AT ROOM TEMPERATURES*

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Abstract

Available thermodynamic data indicate that the cubic modification of carbon is the stable form at room temperatures and pressures above 15,000 atmospheres. Elemental carbon was formed under pressures as high as 35,000 atmospheres by the reaction: mercuric carbide→mercury+carbon. The carbon was identified as graphite by *x*-ray powder patterns.

The experimental procedure was to enclose the mercuric carbide powder in sealed copper cylinders which were compressed by hydraulically operated tungsten carbide pistons in a hollow steel cylinder. The rate of decomposition was unpredictable and more often than not proceeded explosively.

Introduction

The extensive literature on the synthesis of crystalline carbon is exclusively devoted to experiments carried on at elevated temperatures. In most of the methods described the temperatures are so high that it would be impossible to sustain high pressures along with the temperatures for any appreciable length of time because the confining vessel would fail at the temperatures used. Some experimentation, such as Hannay's (1) discredited attempts to produce the diamond, has been done at only moderately elevated temperatures. It should also be noted that the temperature of formation of carbon black is comparatively low but the product does not give *x*-ray diffraction patterns that would warrant its being described as distinctly crystalline.

The available thermo-dynamic data (2) indicate that graphite is the stable form of carbon at all temperatures if the pressure is below 15,000 atmospheres, and that diamond is the stable form at higher pressures, if the temperatures are not greatly above room temperature. The transition boundary at moderate temperatures falls not only well within the limits of convenient laboratory experimentation but also within the range of industrial processes. On the basis of these data Bridgman (3) has unsuccessfully attempted to convert small flakes of graphite to diamond. The failure of an attempt to convert one allotropic form to another does not vitiate the thermo-dynamic data because of the strong tendency of one form to remain in a metastable condition after the transition boundary has been passed. The adaption of such a transformation to practical uses is greatly limited by the particle size of the product if, as appears to be true in this instance, conditions are unfavorable for crystal growth by accretion.

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The objective of this investigation was to discover a reaction, one product of which would be elemental carbon whose rate of formation could be controlled and which would proceed under conditions that would permit crystal growth by accretion. Without describing unsuccessful attempts it can be stated that the reaction: mercuric carbide→carbon +mercury, occasionally fulfills all the above conditions, yielding graphite. However, in most instances the decomposition is either only slight or proceeds explosively. The reaction is well adapted to high pressure experimentation because the carbide is a dry white powder and the liquid product mercury forms a solid amalgam with excess copper thus eliminating many of the difficulties of sealing off gases and liquids under high pressure.

Experimental Procedure

Figure 1*a* is a cross section of the pressure assembly which is actuated by a hydraulic ram. The thrust of the ram is transmitted through the upper solid steel cylinder which drives a tungsten carbide piston $\frac{1}{4}$ inch

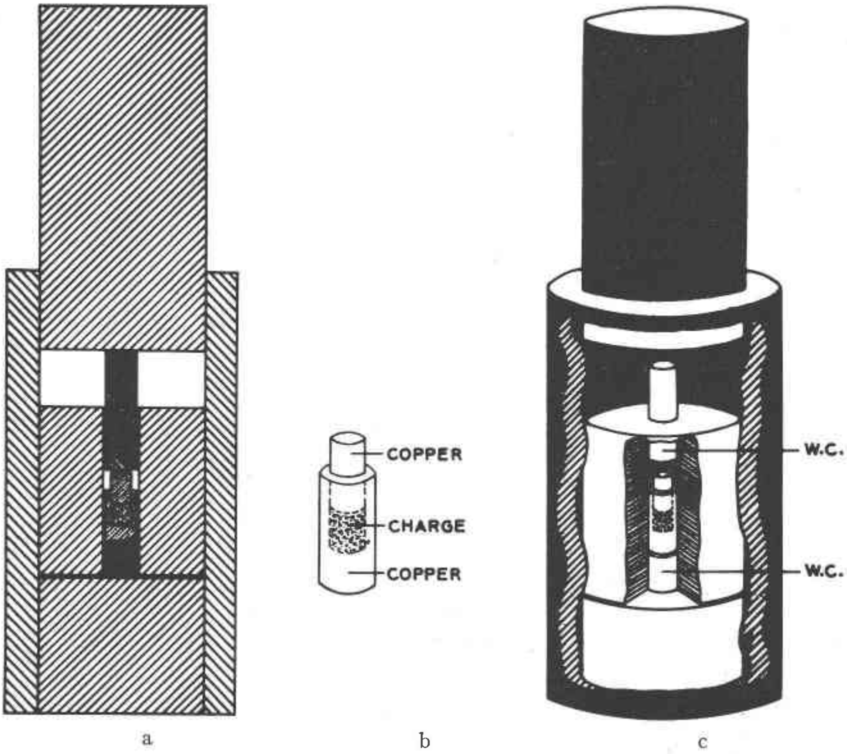


FIG. 1. Pressure assembly.

in diameter into the pressure cylinder. A small tungsten carbide plug closes the other end of the pressure chamber and supports the copper jacketed sample, Fig. 1*b*. The cylinder rests on a solid steel cylinder of the same diameter and all is enclosed in a steel jacket that serves to keep the component parts in alignment and also gives protection from flying chips if the protruding end of the $\frac{1}{4}$ inch piston fails. The sample, approximately one-quarter gram in weight, is placed in a $\frac{1}{4}'' \times \frac{3}{8}''$ drilled copper cylinder, Fig. 1*b*, and a copper plug is inserted in the open end. Under compression the plug cold welds to the wall of the copper cylinder when the yield point of copper is exceeded. Figure 1*c* is a cut-away sketch of the assembly ready to be placed under the hydraulic ram. The several cylindrical surfaces are ground to a smooth sliding fit.

An electrically driven oil pump of 10,000 psi capacity powers the ram through a bypass control valve which can be regulated between 500–6,000 psi. The cross-sectional area of the ram piston is slightly over five square inches which when driving the $\frac{1}{4}''$ diameter tungsten carbide piston gives a hydraulic multiplication of 103. When pressure on this piston exceeds the yield point of copper, the jacket enclosing the sample flows plastically and transmits the pressure hydrostatically to the sample. Tissue thin sheets of copper are extruded 2–3 mm. above and below the tungsten carbide piston between it and the walls of the pressure chamber. In several instances when the steel of the pressure chamber failed the copper flowed into the cracks developed, Fig. 2.

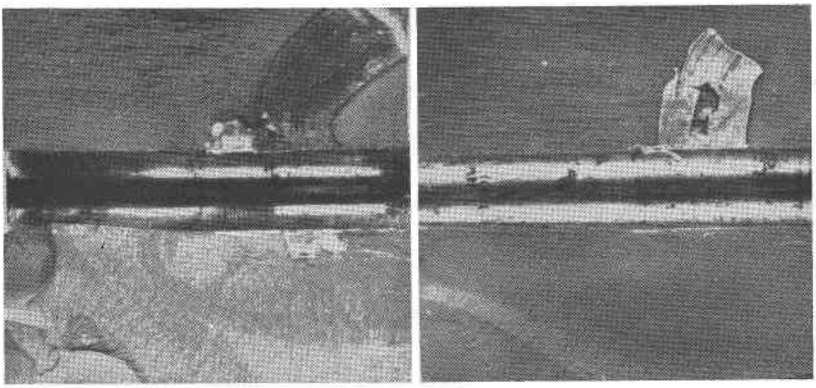


FIG. 2. Halves of steel pressure cylinders that cracked showing tissue thin sheets of copper that were extruded into the cracks.

At the conclusion of an experimental run, the copper case with the enclosed sample is forced out of the pressure cylinder with a hand operated hydraulic press. It is then cut in half by rolling under a knife edge, the sample removed, digested in nitric acid or a solution of potassium cyanide and washed. Graphite when produced was identified by *x*-ray powder patterns. The reaction is highly erratic and unpredictable. Often decomposition proceeds only far enough to darken the sample even after several days under pressure. After dissolving these samples there remains a flocculent black residue too small to be positively identified. Several samples were lost by spontaneous explosions while cutting through the case or while forcibly removing the compacted sample with a needle point. The greatest source of failure which accounts for the loss of three out of four samples is the explosive decomposition while bringing the pressure up to the desired point. This is easily recognized by the sharp sound and the shock which is transmitted to the pressure gauge. If the pressure is sufficiently high at the time of explosive decomposition the pressure cylinder ruptures and a fine black soot is driven into the available openings. The carbon produced by explosive decomposition is too finely divided to give an *x*-ray powder pattern.

On opening the copper cases the first impression, in those instances when graphite was produced, was that it had the high luster of natural graphite. Under the microscope it was apparent that the luster was due to the multitude of minute spherical globules of mercury on the surface. Nitric acid or solutions of potassium cyanide were used to dissolve the mercury and the sample then broke up into irregular fragments with a dull luster and a somewhat porous appearance. These fragments crushed readily but offered more resistance than was anticipated. This first impression of grittiness was lost on crushing. *X*-ray powder patterns gave sharp distinct lines with no evidence of preferred orientation which is so characteristic of graphite. No attempt was made to determine whether both forms of graphite were present.

Discussion

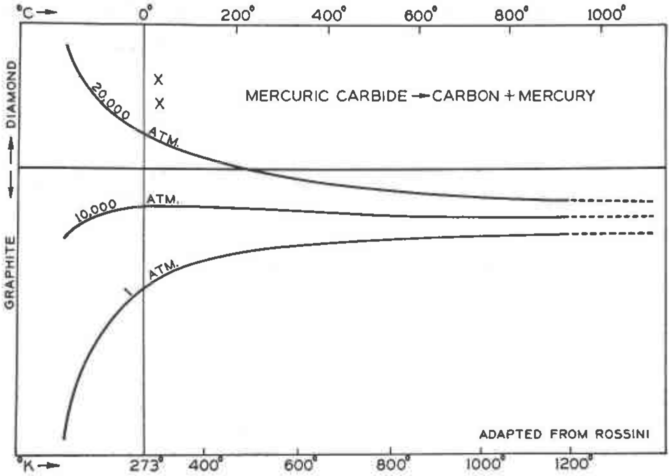
Several methods of preparing mercuric carbide were used, all based on passing acetylene gas into solutions of mercuric salts. Two compounds, HgC_2 and $HgC_2 \cdot \frac{1}{2}$ H_2O have been previously reported. The hydrate would have 3.4% H_2O but its determination is fraught with difficulty because of the tendency of freshly prepared samples to decompose explosively around 100° C. All water however is removed in a vacuum desiccator. One near serious accident occurred in attempting to dry samples of the freshly prepared carbide in an oven at 110° C.

In the early stages of the investigation it was thought that particle size exercised a control over the tendency to explode because rapid precipitation yielded material that exploded readily with increased temperature or pressure. *X*-ray powder patterns from these samples gave broad diffuse lines indicative of minute crystals. Samples prepared by the slow precipation from dilute solutions showed less tendency to explode and gave sharp lines in x-ray patterns. Mercuric carbide precipitated slowly from a dilute $KHgI_3$ solution gave the most satisfactory results and it was from such samples that graphite was produced. However, working under the assumption that particle size controlled the tendency towards spontaneous decomposition, little progress was made toward the preparation of samples from which similar results could be obtained under apparently identical conditions. The experiments were conducted between the temperature range of solid CO_2 and 125° C. and pressures up to 30,000 atmospheres. The results were very erratic and temperature had no apparent influence upon the rate of reaction.

In September 1952 samples which had aged over the summer were found to be stable in the range of pressure and temperature of the previous experiments. They could also be analyzed by distilling over the mercury in a vacuum at 200° C. and after 6 days at 35,000 atmospheres at room temperature decomposition had only proceeded far enough to darken the sample. A reexamination of previous work showed that an hypothesis of stabilization by aging could account for the erratic behavior that had previously been encountered.

Such an hypothesis can appear plausible by assuming that in the rapid precipitation of such a highly insoluble compound many centers of disorder would develop within the crystals because of the rapidity with which the atoms must fall in place. In such a structure with many centers of disorder, each unstable with respect to the whole, a rise in temperature or pressure could initiate decomposition within one which would activate adjacent centers until enough energy was released to detonate the sample. If during the process of aging, time allows the disorder to partially heal and to reach a relative degree of equilibrium, the sample itself may become stable. In experimental procedures in which negative results are the rule and success comes occasionally by accident one must of necessity have recourse to any hypothesis which indicates avenues of further experimentation. In this instance it appears that in well aged samples a controlled rate of decomposition may be attained if they are subjected to somewhat higher temperatures, higher pressure or both.

In Fig. 3, adapted after Rossini (4), the interval between the x's shows the range in which graphite was produced. This is well within the region where diamond should be the stable modification but no conclusions are warranted as to whether these results indicate that the diagram is inaccurate or whether other factors may exercise control over the modification that is formed. It has been suggested that the decomposition of a compound in which the carbon is tetrahedrally bonded in a manner analogous to that of the diamond might favor the formation of



ADAPTED FROM ROSSINI

FIG. 3. Diamond-graphite phase diagram.

the cubic modification. The structure of mercuric carbide is similar to that of calcium carbide and the dissimilarity of the structure to that of diamond may militate against its success. However, carbon is appreciably soluble in mercury (5), especially at higher temperatures, and hence this reaction may afford the possibility of crystal growth by accretion.

The few positive results of the investigation bear little relationship to the time and effort expended. A serious handicap to one considering the synthesis of the diamond is the meager information available about the negative results of the innumerable attempts that have been made in the past few decades. Much of this past work has been at extremely high temperatures and without doubt there has been a great deal of duplication of effort. The evidence afforded by the natural occurrence of diamond indicates that the temperatures of formation were not greatly in excess of 1000° C. The existing thermodynamic data support this conclusion.

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