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THE DEPOSITION OF PYROLYTIC GRAPHITE

by

R. J. Diefendorf

Report No. 60-RL-2432M

May 1960

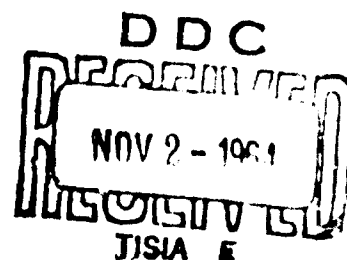
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THE DEPOSITION OF PYROLYTIC GRAPHITE

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Published by
Research Information Section
The Knolls
Schenectady, New York

ABSTRACT

The study of the deposition processes in pyrolytic graphite, made from the gas phase, has been largely empirical. The work to be presented attempts to show that the deposition is controlled by reactions in the gas phase. Experiments have been performed at fast and slow rates of growth using natural, pyrolytic, and commercial graphites as substrates. The deposition processes which are occurring at various temperatures and pressures for all three substrates are described.

Manuscript received April 22, 1960.

THE DEPOSITION OF PYROLYTIC GRAPHITE

R.J. Diefendorf

I. INTRODUCTION

Pyrolytic graphite has been produced for many years by thermally decomposing a carbonaceous gas on a hot surface.⁽¹⁾ Even though the material is very old, the properties of pyrolytic graphite have only been measured recently. Brown and Watt⁽²⁻⁴⁾ described the properties of pyrolytic graphite deposited over the temperature range of 1600° to 2100°C. More recently, Brown, Clark, and Eastabrook⁽⁵⁾ extended the data to include materials made at temperatures as low as 1200°C.

The study of pyrolytic graphite has been largely empirical, and little work has been done on the deposition processes except by Meyer,⁽⁶⁾ and by Kinney^(7,8) and co-workers. Thus the variation in the properties of pyrolytic graphite deposited at different temperatures, as measured by Brown and Watt, have never been related to differences in the deposition processes. This is not surprising, for in most previous studies,^(2-5,9) data were collected under conditions where both gas-phase and surface reactions were occurring simultaneously and in apparatus in which large temperature and concentration gradients were common. The understanding and the mathematical description of such experiments with complex geometries is very complicated. It involves knowing the rate constants for all the reactions, the thermal diffusivities, the diffusion coefficients and the accommodation coefficients for all chemical species in a dynamical gas system. This information is not available. This report gives the results of some simple crystal growth experiments which were performed to understand the deposition processes. These results show that the structure and growth of the deposit depend on the reactions which are occurring in the gas phase.

II. EXPERIMENTAL

The apparatus consisted of a cylindrical metal vacuum chamber containing a resistance-heated graphite rod along the axis of the cylinder. Sight ports, gas inlets, and vacuum lines were placed at appropriate points in the vacuum chamber, such that the flow and pressure of the gas as well

as the temperature of the graphite rod could be controlled and measured. The graphite rod was 2.5 mm in diameter with a reduced central section 25 mm long and 1.7 mm in diameter. This configuration was found to give a constant temperature, when measured with an optical pyrometer, over 18 mm of the 25-mm-long center section of the heated rod. Since some of the experiments were performed at low pressures, Teflon "O" rings were used at seals instead of the usual neoprene "O" rings, for it was found that the neoprene rings degassed badly.

For the experiments which were performed at 800°C, the metal apparatus was found to leak too rapidly. The experiments were therefore made by placing the graphite specimen in a silica tube and putting the silica tube in a resistance-heated furnace.

The densities were measured by a sink-float technique.

III. RESULTS AND DISCUSSION

A. Deposition on Natural and Pyrolytic Graphite

At very low supersaturations, a graphite crystal with nearly perfect basal planes should be expected to grow on the edges of the basal planes.⁽¹⁰⁾ To test this hypothesis, a rock containing large flakes of graphite was broken to expose new surfaces on the graphite flakes. The size of the flakes was of the order of 6 x 6 mm, but actually consisted of a number of smaller crystals about 1 mm in length and width. Angles of 60° and 120° were observed at the corners of these crystals. One fragment of rock with a flake of graphite was carefully observed, and the dimensions of a crystal were measured under a microscope. This was then placed in a silica tube and heated in a vacuum of 10^{-5} mm Hg to 1000°C and then cooled to 800°C. Purified methane was then flowed through the system for two weeks at about 9.1 mm Hg. Upon cooling, it was observed that no detectable growth had occurred on the basal plane. Since the basal plane edges of the crystal were bounded by other crystals and the rock, no growth could occur there, but at several boundaries between crystals triangular sheet-like growths grew out into space. Some grew out at angles of about 20° and others at about 60° from the basal planes. This observation of course suggests twin growth from the edge of the basal planes.⁽¹¹⁾ It should be remarked that the silica tube and the rock which served as a substrate for the graphite flake were coated with adherent coats of carbon. Apparently these surfaces offered enough traps for gaseous decomposition products that the supersaturation of the gas was maintained at a level insufficient to nucleate the basal planes of the graphite.

This result is in agreement with those of Meyer⁽⁶⁾ who found that no carbon would deposit on a well-graphitized filament of pyrolytic graphite, unless the pressure in the apparatus was increased to a high enough value to cause nucleation on the filament. Once nucleation had occurred, decomposition of the gas on the filament occurred regardless of the pressure. It should be realized that his pyrolytic filament presented "C" surfaces to the gas which were probably highly perfect due to the graphitization treatment.

A rather similar but revealing experiment on the difficulty of nucleating growth on a "C" surface was the following: A 0.025-mm-diameter carbon filament was given a thin pyrolytic carbon coating and then graphitized. A 2.5 mm length of this was then heated to 1600°C in 1 atmosphere of methane. No growth was observed to occur for 2 days, but suddenly rapid growth occurred for about 15 seconds before the end of the filament burned out. During this short time, the diameter of the filament increased to 0.525-mm diameter. Thus until nucleation occurred on the filament, it was unable to grow.

In contrast with the natural graphite in which the basal planes are relatively perfect, commercial graphites and "as-deposited" pyrolytic graphites undoubtedly have highly imperfect structures. In particular, the growth on the basal planes of pyrolytic graphite should be facilitated at crystal boundaries. With such structures, it should be expected that growth will occur on the "C" surfaces at low supersaturations, and a specific experiment was devised to test this hypothesis. Pyrolytic graphite was used since the high degree of orientation makes measurement of the growths easy and microstructure observations unambiguous. A 1/8-inch-square bar of pyrolytic graphite made at 2550°C was resistance heated to 1600°C in methane. The methane pressure was adjusted so that the ratio of the mean free path to radius of the apparatus was about one third. The surprising result was that although "C" surface growth occurred, no growth occurred on the "A" surfaces [Fig. 1(a)], indicating that the "A" surfaces were poisoned. In order to eliminate the possibility of the latter effect, in a second experiment, the surface of the rod was first etched away with hydrogen, and then methane was admitted at the same pressure as in the first experiment. It was now observed that "C" surfaces grew as before but that "A" surfaces also grew, although quite unevenly [Fig. 1(b)]. The growth on the "A" surface was still slower than on the "C" indicating that the surface was probably not completely cleaned by the hydrogen treatment.

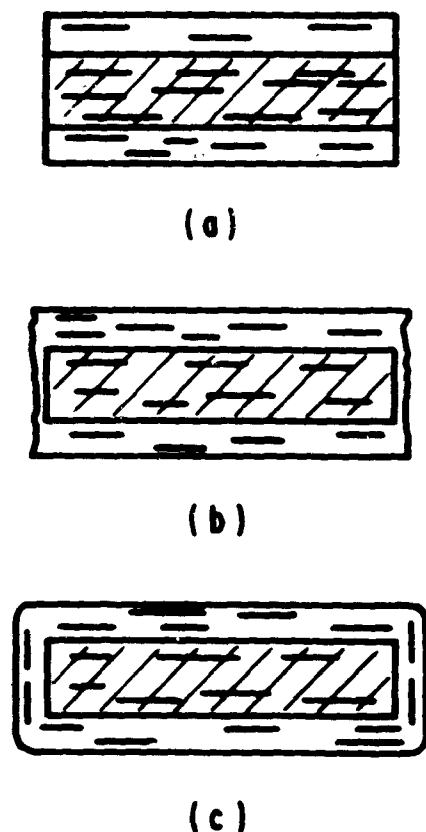


Fig. 1 The cross sections of pyrolytic graphite deposits on pyrolytic graphite substrates. The hatched areas show the initial pieces. (a) At low supersaturations, an unetched substrate coats only on the basal planes. (b) If the substrate is etched with hydrogen prior to deposition at low supersaturations, deposition can occur on all surfaces, but the coating has the same crystallographic orientation as the substrate. (c) At high supersaturations, the substrate is coated on all surfaces, but the coating is deposited such that the C-axis is always normal to the surface.

Finally, a bar of pyrolytic graphite was heated to 1600°C in methane at a much higher pressure of 5 mm Hg. Here, growth was observed to occur on all surfaces with the C-axis of the coating normal to the deposition surface [Fig. 1(c)]. This orientation of the C-axis implies that two-dimensional noncoherent nucleation⁽¹²⁾ is occurring, or that large aromatic compounds are involved in the coating process. By two-dimensional noncoherent nucleation, it is meant that a crystal nucleus is formed on the substrate by an atom by atom addition, but which has no specified crystallographic relationship to the substrate. In the second case, large aromatic molecules, which are formed in the gas phase, are assumed to plate out on the substrate surface and thus form a nucleus which at low temperatures will be unoriented with respect to the substrate. Further growth, for both cases, would be the same and would consist of atom by atom addition to the nucleus. It is not known which of these processes is occurring in the experiment described. However, experiments are being performed to determine which is the important growth process. Since it is not understood which of the two processes occurs, whenever two-dimensional noncoherent nucleation is subsequently used in the text, the author means that at least one of these two processes is occurring.

B. Deposition on Commercial Graphite

The deposition of pyrolytic graphite on commercial graphite rods has been studied under two sets of conditions. In one group of experiments, the methane pressure was held low enough so that a low deposition rate was obtained, but high enough so that two-dimensional noncoherent nucleation or the formation of large aromatic compounds occurred. The second group was performed at a higher pressure of methane such that some of the deposition rates were high. These experiments closely paralleled those of Brown and Watt.

At low pressures, simple crystal growth theories predict that if two-dimensional noncoherent nucleation is occurring, the density of the deposit should be essentially constant over the whole temperature range of deposition. (Perhaps a slight increase in density should be expected with increasing temperature due to the ordering effects of increased thermal energy.) The same result would also be predicted from the deposition of large aromatic molecules. In both processes, the deposit should be turbostratic.

These low-pressure experiments were run at a pressure of 17 microns of methane. (This corresponds to a ratio of the mean free path of the methane molecules to the radius of the apparatus of about 1/10.) The results of these experiments are indicated in Fig. 2. The C-axis orientation, except for the 800°C run, was found to be normal to the surface as predicted. Furthermore, except for the 800°C run, the layer stacking in these low-pressure deposits were highly turbostratic with a corresponding increase in the C_0 .

The run performed at 800°C at low pressure is somewhat anomalous as the material had a density very close to the theoretical. X-ray diffraction experiments confirmed this high density as the C_0 spacing was 6.708 Å and the structure was highly ordered three dimensionally. Part of the difference between this experiment and the other low-pressure experiments may have been caused by performing this experiment in an externally heated silica tube and at a higher pressure of 1 mm Hg of methane. In distinction from the other runs where the C-axis of the coating was found to be normal to the outer surface, it was impossible to find the interface between the pyrolytic graphite and the commercial graphite substrate. Yet the microstructure of the uncoated commercial graphite and the pyrolytically coated commercial graphite was substantially different, indicating that deposition has occurred in the commercial graphite.

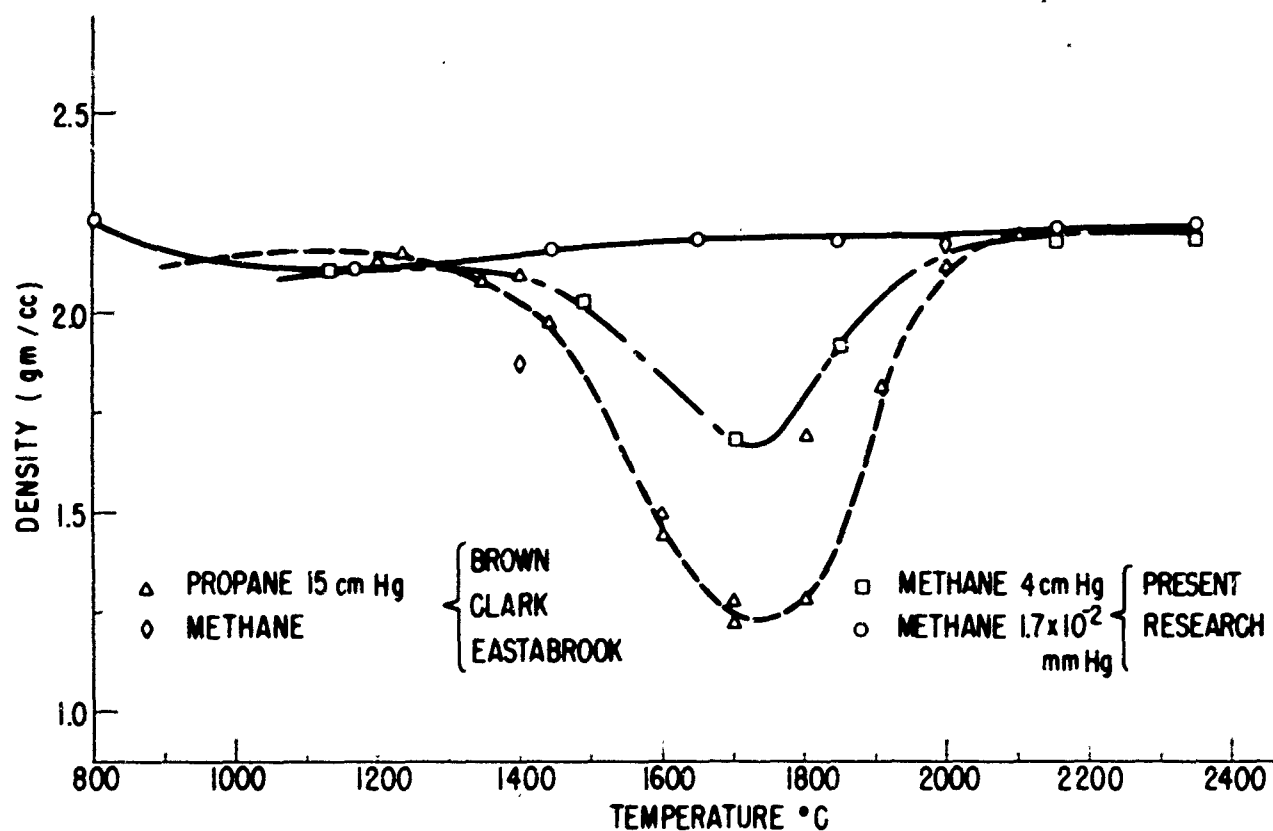


Fig. 2 The room temperature density of pyrolytic graphite as a function of deposition temperature.

The second set of experiments was performed at high pressures (5 mm Hg) of methane, and the room temperature density of the deposits is shown in Fig. 2. These densities agree with the densities reported in a recent paper by Brown, Clark, and Eastabrook. The differences in density which are observed should be expected, since the geometries of the apparatus differed somewhat.

The most striking difference between the high- and low-pressure runs is the drop in density observed in the mid-temperature range of the high-pressure experiments. These lower densities would appear to have been caused by the formation of particles in the gas phase which are subsequently incorporated in the coating. Evidence for this is in Figs. 3 and 4, which show fracture surfaces of pyrolytic graphite. The material illustrated in Fig. 3 was made at low pressure with no soot formation. Its structure shows the typical slate-like fracture pattern of graphite. The material which is shown in Fig. 4 was made with such a high-pressure of methane that soot was observed to form in the gas phase

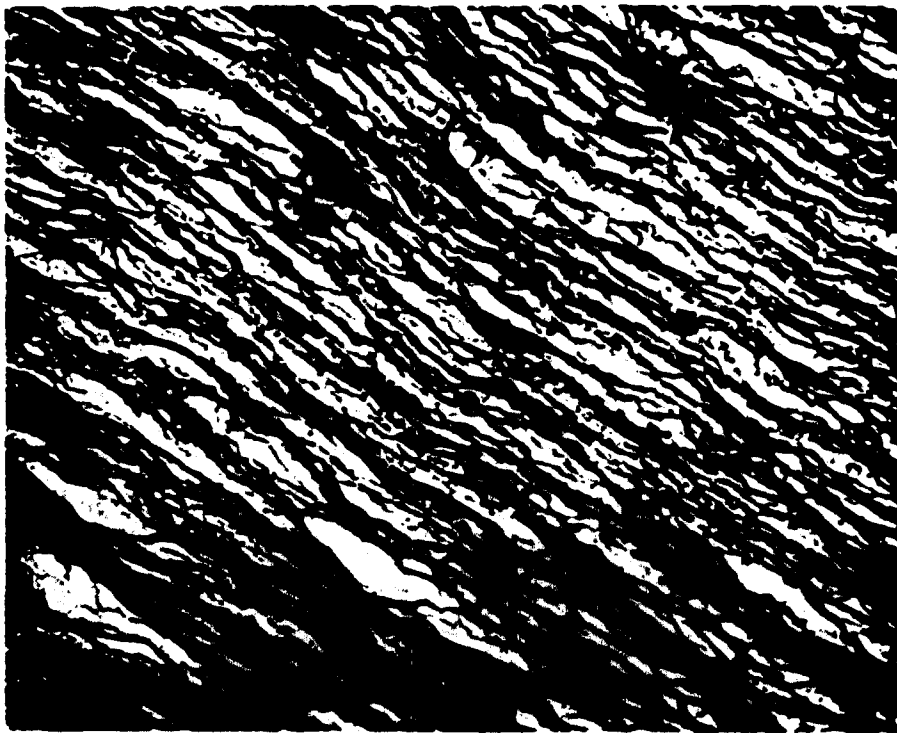


Fig. 3 An electronmicrograph of a fracture surface of a nonsooty pyrolytic graphite deposit. A carbon replica of the fracture surface was made and shadowed with chromium. 5,000X

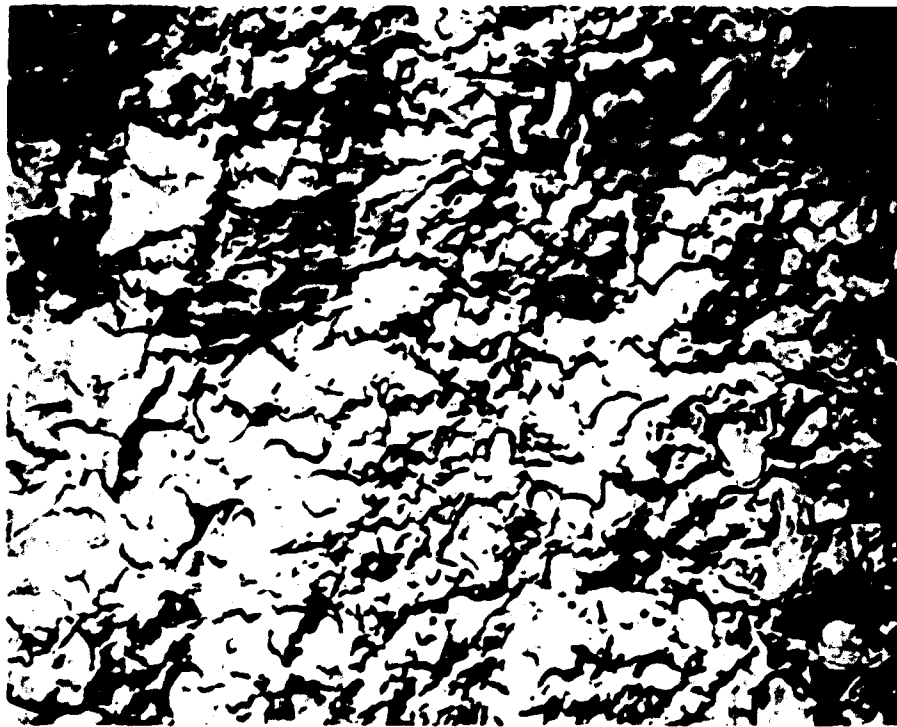


Fig. 4 An electronmicrograph of a fracture surface of a sooty pyrolytic graphite deposit. A carbon replica of the fracture surface was made and shadowed with chromium. 5,000X

throughout the run. In contrast with the slate-like fracture surface of a nonsooty pyrolytic graphite, this figure shows the typical fracture pattern when soot particles are present in the deposits.

The conjecture that the formation and incorporation of soot give the low densities over the mid-temperature range of the experiments performed at high pressure leads to the assumption that perhaps the gas-phase reaction is not really much different from the surface reaction. The deposition of additional material on a gas-phase suspended particle would not appear to be radically different from that on the surface. Quantitatively, both the relative size of the particle and the coating surface must be considered, but the qualitative argument is not affected. However, the real problem is whether the structure of the gas-phase particle is similar to the surface structure of the substrate. At high growth rates the structures are probably highly different, but at low growth rates they are probably similar.

The geometry used in the present study and by Brown, Clark, and Eastabrook makes it difficult to interpret what is occurring in the high-pressure experiments. This geometry, which has a heated graphite rod axially located in a metal cylinder with cold walls, results in large temperature gradients and at high temperatures, concentration gradients which must be considered when explaining what is occurring. Nevertheless, one can speculate on what should occur by reference to the deposition processes which were observed to occur on pyrolytic graphite as reported in section III-A.

At low temperatures, the temperature will drop to a value where the gas-phase reaction is very slow in just a short distance from the surface. Decomposition of the carbonaceous gas can only occur at the surface or close to the surface of the graphite rod, and there will be a negligible concentration gradient in the system. Under such conditions, small aromatic compounds should be formed in the hot sheath of gas around the heated rod. However, their growth should be small, since the number of collisions made before they are plated on the heated rod will be small. The cold walls will remove any of these products which diffuse away from the filament. The process is essentially the same as that which occurs in the low-pressure experiments and is not complicated to understand. Kinney and co-workers⁽⁷⁾ have measured the activation energy for the deposition rate over this temperature region and find it is equal to the energy required to break the weakest bond in the starting material.

At higher temperatures, the reaction zone around the hot graphite rod increases in width. Close by the filament, the reaction will be quite fast due to the higher temperature, but the species which are formed do not have a large distance to diffuse until they reach the surface of the rod and thus are small in size. Products which are formed farther away from the rod do have to diffuse a longer distance to the rod. Under these conditions, a concentration gradient in carbon will be formed, with a minimum in carbon concentration at the surface of the rod. At these temperatures where initial breaking of the bond in the starting material is still the rate controlling step, there will be formation of relatively few large aromatic products in the gas phase, but these will continue growing catalytically, as in the low-pressure experiments described in section III-A, until they are removed from the system.

If these particles are not removed before they reach critical size, soot will be formed. It is assumed that this critical size is that at which two-dimensional noncoherent nucleation of additional layers can occur on the particles. The formation and subsequent incorporation of these particles into the deposit predicts certain consequences. They are: (1) the deposit should not graphitize easily since the geometrical conditions limit the amount of crystal growth that can occur; (2) the density of the deposit should be lower because of the anisotropic thermal expansion coefficients. The deposits made in the mid-temperature range have these properties.

At the highest temperatures of deposition, several considerations other than the crystal growth must be taken into account. First, appreciable movement of particles will occur at the surface tending to increase the density. Second, the equilibrium carbon vapor concentration is higher at these temperatures; thus the driving force is lower. At these high temperatures, Brown and Watt have found that the energy of activation for the deposition averages 21 kcal/mole for methane, a value which is much too low for bond scission in the raw hydrocarbon. Thus, the prime reaction is not rate controlling any more. This means that the buildup of gas-phase particles will be quite different from the ones at lower temperatures. From both crystal growth and polymerization theory, it should be expected that at these high temperatures many large hydrocarbon molecules should form, but with a smaller average molecular weight than those formed at lower temperatures. Therefore at lower temperatures, a small number of large aromatics are formed, and at high temperatures a large number of small aromatics are formed. It might be expected that these aromatics formed at high temperature are

too small and are in a region where the carbon concentration has been lowered to too low a value to have two-dimensional noncoherent nucleation occur. Furthermore, as these small aromatics diffuse into the hotter regions around the hot graphite rod, they are unstable with respect to acetylene and graphite, and so a slow growth of some of the aromatics should occur as well as the decomposition of others. Hence, the growth process is not much different from that for the low-pressure experiments. The net effect is that a more perfect structure should be formed as is indicated by the increase in density of the deposits.

While the above is highly speculative, the reasoning does not disagree with the growth processes observed in section III-A. If it is admitted that the reaction on gas-phase particles is not fundamentally different from that of the bulk surface reactions, then the general density curve values obtained from materials deposited at high pressures can be found.

IV. CONCLUSIONS

The structure and growth of pyrolytic graphite is largely controlled by the gas-phase reactions. At very low pressures of pyrolysis gas, graphite with relatively perfect basal planes appears to grow only on the edges of the basal planes. With materials which are somewhat imperfect, such as ungraphitized pyrolytic graphite, growth can occur on the edges and on the surface of the basal planes at low pressures. These pressures are so low that effectively the gas-phase reaction which produces soot and higher polymers is stopped. At slightly higher pressures where the gas-phase reaction becomes important, nucleation of new layers will occur on the graphite substrate. As long as the gas pressure is relatively low, the growth of the gas phase suspended particles will be slow, and correspondingly as in an slow crystal growth the structure of the deposit will be highly ordered. Thus the density of the deposit will be high, but because of noncoherent nucleation, the structure will be turbostratic. Any further increase in pressure will result in poorly formed particles being formed in the gas phase. The subsequent incorporation of these particles in the deposit will give a low density. At certain gas pressures, these gas-phase particles will be coated in the gas to further change their structure. The exact value of the density of the deposit obtained for any temperature and pressure is strongly a function of the geometry of the apparatus.

ACKNOWLEDGMENTS

The author gives thanks to G.W. Sears, J.H. Westbrook, and J.E. Burke for their many helpful discussions.

REFERENCES

1. W.E. Sawyer, U.S. Patent No. 229,335 (1880).
2. A.R.G. Brown, A.R. Hall, and W. Watt, *Nature* 172, 1145 (1953).
3. A.R.G. Brown, W. Watt, R.W. Powell, and R.P. Tye, *Brit. J. Appl. Phys.*, 7, 73 (1956).
4. A.R.G. Brown and W. Watt, Industrial Carbon and Graphite, Society of Chemical Industry (1958), p. 86.
5. A.R.G. Brown, D. Clark, and J. Eastabrook, *J. Uncommon Metals*, 1, 94 (1959).
6. L. Meyer and R. Gomer, Third Biennial Carbon Conference, Pergamon Press (1959), p. 425.
7. D.B. Murphy, H.B. Palmer, and C.R. Kinney, Industrial Carbon and Graphite, Society of Chemical Industry (1958), p. 77.
8. J.S. Conroy, R.S. Slysh, D.B. Murphy, and C.R. Kinney, Third Biennial Carbon Conference, Pergamon Press (1959), p. 395.
9. R.O. Grisdale, A.C. Pfeister, and W. VonRoosbroeck, *Bell System Tech. J.*, 30, 271 (1951).
10. G.W. Sears, *J. Chem. Phys.*, 31, 358 (1959).
11. C. Palache, *Am. Mineral.*, 26, 709 (1941).
12. G.W. Sears, *J. Chem. Phys.*, 31, 157 (1959).

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Title Page

AUTHOR Diefendorf, R.J.	SUBJECT CLASSIFICATION graphite	NO. 60-RL-2432M DATE May 1960
TITLE The Deposition of Pyrolytic Graphite 34-6110		
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DEPARTMENT: Metallurgy and Ceramics Research