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CARBON AND GRAPHITE

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I. Introduction

A. GENERAL INFORMATION

Every element or material has some particular characteristic or group of characteristics that sets it apart from any other material. Those of carbon and graphite are the subject of this chapter, as are the means of

developing and exploiting these characteristics in certain commercial areas.

The earth's crust contains somewhat less than 0.2% of carbon, most of it as coal, organic materials, graphite, diamond, and carbonate minerals. Since the crust also contains about 50% oxygen, it seems reasonable to assume that the major part of the carbon present in the crust during prehistoric cooling was in the form of carbon dioxide and carbon monoxide, depending on the temperature of the equilibrium. When life was formed, the life processes began to use up most of the carbon dioxide in the atmosphere and to put the carbon into the microorganisms or early forms of plant and animal life; and part of the oxygen was returned to the atmosphere. Natural graphite is often found in connection with carbonates and other carbon compounds and could be the result of their decomposition under conditions of high pressure and high temperature. The source of carbon in diamonds is not clear, since they usually appear in the blue earth cores of extinct volcanoes, although they could have had organic origin. Although certain details are speculation, it is true that the major part of the carbon in the earth's crust has come through the life cycle and been involved in complex organic compounds.

To nature's supply of coal, diamonds, and natural graphite, man has added a number of industrial processes for making synthetic forms of carbon.

Because of the wide variety of organic compounds available to form chars, the latitude available in char-forming processes, and the low mobility of carbon atoms at charring temperatures, we can make different materials which can be engineered or constructed to meet a wide range of requirements. Neither graphite nor carbon can be melted in commercial processes to eliminate the structure, owing to its past history. In fact, the solution of carbon in iron and its subsequent precipitation as powdered graphite, the formation of pyrolytic carbon from carbon-containing gases, and chemical reactions are the only means of eliminating the traces of its past history from a sample of the material. The distinctive properties of carbon from particular sources are used to advantage in the manufacture of industrial carbon and graphite and make possible a wide variety of physical characteristics.

Important results of these facts are that perfect crystals of graphite are very rare indeed, and the imperfections and grain boundaries present in the materials are as important in determining the properties of a sample of material as are the properties of the perfect crystal. Impurities and adsorbed gases also play an important role. Many of the important characteristics of graphite and carbon depend on the surrounding atmosphere and on impurities in the material. A graphite brush, seal,

or bearing that operates quite properly under normal atmospheric conditions can fly off into a cloud of dust when water vapor and oxygen are removed, unless special adjuvants are added.

The wide variety of materials and the many ways of achieving special properties have resulted in an industry that has deserved the name of "black art," given it by some of the users of carbon and graphite. This has been true in the past and is still true in certain areas where successful operation on specific applications is due to some detail in a process that could not be protected by patents or revealed by analysis. The strong activity of the Atomic Energy Commission and its various sub-contractors in the field of nuclear graphite has opened up a large area of graphite technology to the public domain. The work supported by the National Aeronautics and Space Administration and its predecessors is also adding to the information in this area. The growth in the number and kinds of publications in the field of graphite materials for nuclear, missile, and space uses tends to confirm the statements made above.

It is not intended that all the possible applications and uses of carbon will be covered in this chapter. Whole industries are built around the adsorption properties of carbon, around natural and artificial diamonds, and around carbon black and lampblack materials. Carbon in composition resistors and pyrolytic carbon resistors, and in industrial composition and ceramic resistors, involves extremely specialized applications. These fields are not considered here.

B. CRYSTAL AND ELECTRONIC STRUCTURE OF GRAPHITE (6, 7, 9, 13, 34)

One of the characteristics distinguishing one material from another is its crystal structure, and this is in turn determined by the distribution of electrons in the outer shell of the individual atoms. Carbon has four such electrons and can form two kinds of crystal: diamond and graphite. We shall discuss here only the crystal structure of graphite.

The ideal graphite crystal has the highest entropy at ordinary temperatures of any form of carbon. The variations from this ideal can be considered in connection with the specific properties of graphite and carbon.

Figure 1 represents the nominal description of the natural graphite perfect crystal. It is approached artificially by precipitation from the carbides (kish from iron carbide), and by annealed pyrolytic graphite. Such a perfect crystal is characterized by a certain sequence in the relative position of the closely bonded basal planes of atoms, called *ab*-planes. Successive *ab*-planes in the ideal crystal are displaced relative to one another, so that every other plane fits exactly over the first. Such a succession may be labeled an *ABAB* sequence. There are other ways of

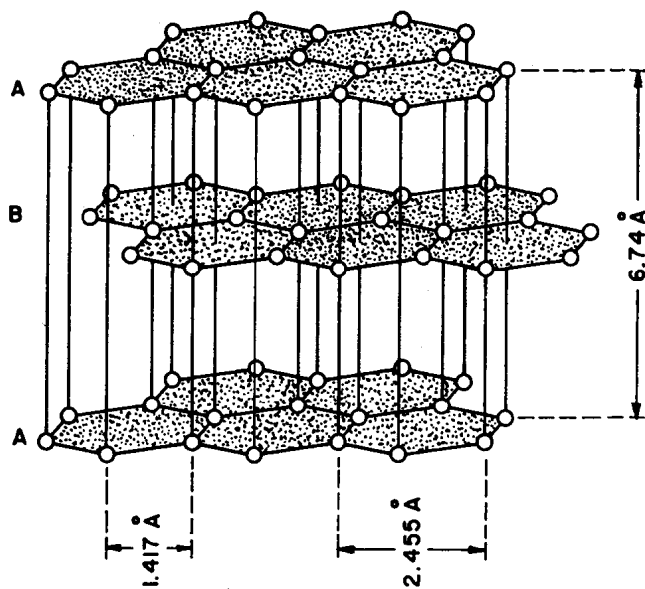


FIG. 1. Crystal structure of graphite.

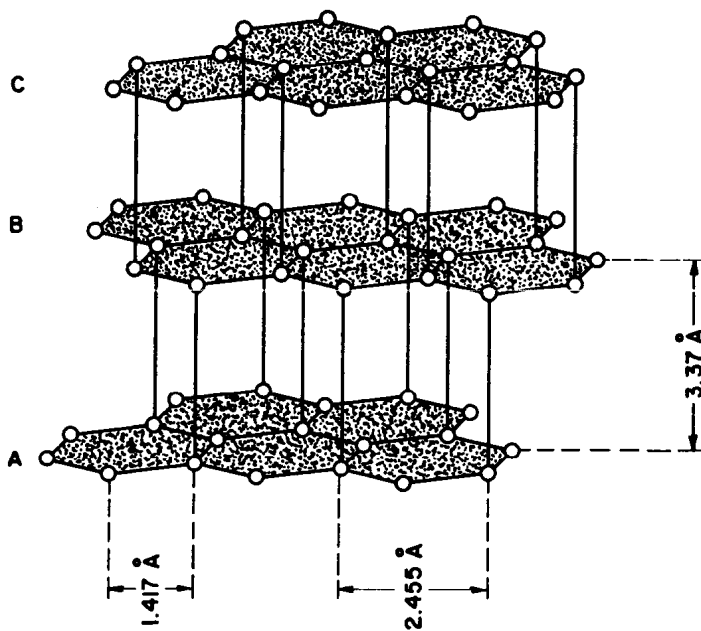


FIG. 2. Crystal structure of graphite—rhombohedral.

stacking the *ab*-planes. For example, Fig. 2 shows the rhombohedral structure of material appearing to a certain extent (up to 30%) in natural graphite in which the *ab*-planes are ordered on the average as ABCABC. The proportion of the rhombohedral form can be increased in natural graphite by strong milling operations and restored to ABAB by heating.

A new form of cubic crystalline graphite has recently been reported by Aust and Drickamer (70), formed by pressing single crystals of natural graphite at pressures above 150 kilobars. It has a unit cell edge of 5.545 Å and a density of 2.80 gm/cm³. The electrical resistance increases by a factor of about 100 in the *ab*-direction and 10 in the *c*-direction.

There are two basic types of defect that cause actual graphite crystals to differ from the ideal presented in Fig. 1. These are layer-stacking defects, in which the *ab*-planes are displaced linearly and angularly in their own plane from the ideal (turbostratic defects), and carbon network bond defects within *ab*-planes themselves; these consist of holes, edge defects, screw dislocations, twinning, chemical defects, radiation damage, and partially graphitized carbon. The forces that hold the layer planes together are van der Waal's forces, which are only about one-twentieth as strong as the chemical bonds between atoms in the layer planes. Therefore, the tendency or urgency for these layers to orient themselves perfectly is not great and does not become effective except at high temperatures (~1600°C). On the other hand, the high binding energy of the atoms in the layer planes makes them stable when formed, and also permits only slight mobility to correct errors even at high temperatures. This is why gas carbons—carbon black and lampblack—cannot be "graphitized"; that is, they cannot be changed to soft, unctuous graphite, whereas many chemicals, like anthracene, which contain the benzene ring structure readily "graphitize."

The electron structure of the carbon atom is such that it wants to form planes consisting of hexagonal benzene rings by means of chemical or covalent bonds in which the strength is of the same order as that of the diamond lattice. This hexagonal structure is in evidence in even the most disoriented amorphous carbon black. The aromatic carbon ring is held together by covalent bonds in which three of the electrons in the outer shell of each carbon atom, called σ -electrons, are "hybridized"; that is, they produce bonds of equal strength even though they belong to different orbitals in the free atom.

These covalent bonds hold any atom in the plane with an energy of about 10.5 electron volts (ev), compared with 10.4 ev for an atom in

the diamond lattice. The additional electron of the L -shell, the so-called π -electron, moves in and around the rings and contributes to the bonding between planes. It is particularly responsible for the electrical properties of graphite. Although the π -electrons are in a filled band well above the σ -electrons, this band partially overlaps to the conduction level, and there are always enough electrons in the conduction level to produce considerable electrical conduction. As will be pointed out in detail later, the electrical conductivity is strongly anisotropic, since the π -electrons can move readily in the layer planes but require higher energy to jump from plane to plane—that is, to move in the c -direction. The heat conductivity is also anisotropic in the same direction, not because of the electron mobility, but because the heat conduction in graphite is due to crystal vibrations or waves (phonons) which are propagated primarily along the layer planes and very little in the c -direction. We have, therefore, in graphite a material that might be called a metal in two dimensions and a nonmetal in the third.

This general picture of an ideal graphite crystal having been described, the deviation from this ideal in available materials will next be considered.

Some of the more nearly perfect natural graphite crystals are only a few millimeters on a side, and it is on these that the best measurements have been made. The recently synthesized pyrolytic types of graphite can now be made in the form of crystals which are as good and very likely will eventually be larger and more uniform than those from any other source. These all conform to the description given in Fig. 1.

Although natural graphite and pyrolytic graphite have their places in industry, the forms most extensively used are called "artificial graphites." They consist of a mixture of graphitic crystals and turbostratic structures containing in addition a certain amount of still more disoriented carbon. The latter may be grain-boundary material originating from organic compounds which generate no hexagonal orientation. Over 50% of the carbon in artificial graphites has the layer structure shown in Fig. 1. The remainder of the material is composed of the basal ab -planes in various stages of orientation and of disordered boundary groups.

As a result of this versatility in crystal structure, graphites can be made to have a variety of properties. How to obtain carbon products of various qualities is the burden of the next subsection. Then the properties themselves will be considered.

It should be noted that natural graphite in powder form, which comes primarily from Madagascar, Ceylon, Central Europe, and Mexico, represents only a small part of the industry economically. Since it is available only in small pieces which must be milled to a relatively fine

powder, it is used primarily where its particular unctuous characteristic is required as an addition to other materials (65).

C. MANUFACTURE OF CARBON AND GRAPHITE

The choice of the initial raw materials (petroleum coke, powdered graphite, pitch coke, petroleum pitch, coal-tar pitch, coal tar, needle coke, etc.) needed to arrive at the desired product is made on the basis of availability, cost, and final requirements. These, as well as the processing variables, control the final cost and properties of the product. The two most important of these factors which determine the extent of final graphitization are the nature of the raw materials and the graphitizing temperature.

In many important applications the approach to ideal graphite crystals is not desired and materials are purposely designed to prevent complete graphitization. For some electrographitic brushes and for certain seal and bearing applications, a partial graphitic structure is desired because it can have better wear characteristics. This result is achieved again by the choice of raw materials, this time primarily from among the blacks and chars of nonaromatic as well as of aromatic compounds, and the processing variables. Combinations run the gamut of crystal structures, from those that approach closely to the ideal crystal, to those that contain no graphite and are not even baked at temperatures high enough to promote any crystal growth ($\sim 1600^{\circ}\text{C}$). Materials baked at temperatures too low for graphitization are called carbon graphite or carbon materials, depending on whether there were any graphite particles in the original mix. Materials baked at temperatures above 1600°C are called electrographite.

Much of the basic information on the manufacture of carbon and graphite materials is available in the literature; the brief summary given below will, however, be helpful in studying possibilities of future developments in these materials.

The processing of carbon and graphite is carried out in a series of well-defined steps which includes these:

1. Choice of Raw Materials

Considering the wide range of possible starting materials and the range of properties required in the final products, it is apparent that the choice of raw materials and the control of their sources are important. The type of carbon in the final product is determined by the specific application, the choice usually being made as a result of extensive tests and development work. Some of the raw materials, such as retort coke, pitch, and petroleum coke, are themselves by-products of other com-

mercial processes; in regard to these, the carbon manufacturer must be able to adapt his processes to the variations inherent in the other processes. Such items as impurities and particle size in natural graphites, particle structure and adsorption in carbon blacks, amount of carbonization in pitch, and ash, particle size, and chemical impurities in coke must all be taken into account, and adjustments must be made in the processes to permit the optimum use of available materials.

2. Preparation of Raw Materials

Very few of the basic raw materials are used directly as obtained. Some may be processed for use by a supplier of carbon raw materials; with others, this is done by the manufacturer. The economics of dealing with large and small quantities determine the details for any particular material. The primary operations involved in this preparation include grinding or milling to meet particle size requirements, calcining (heating to a temperature high enough to remove volatile materials which might be left in during the process of formation), and the preparation of grog (material that is mixed, baked, and ground) to be mixed in again with new material as is done in the ceramic industry. Because many of the details of the processes in which solid carbon is formed are not under the control of the carbon manufacturer, he must use his knowledge of the processes to provide a uniform end product.

3. Mixing

The operation of mixing the raw materials, which are usually heavy liquids and light powders, is usually carried out in sigma mixers; these are similar to large bread mixers. Steam- or oil-heated jackets provide the heat to melt the pitch, and the amount of pitch and the temperature are adjusted to give a strong kneading action. The provision of too little binder results in a dry, powdery mix in which the powder and binder are not forced into intimate contact. Too much binder results in a wet, sloppy mix which leads to excessive shrinkage during subsequent baking. Mixing time is adjusted to give the best results in extrusion, molding, or pilling—whichever the next process may be.

Ball mills are also used for mixing in certain special cases where very heavy mechanical forces are required. This usually occurs when it has been necessary to add enough solvent to dissolve certain resins, and the mix is therefore very wet, or else with exceptionally dry mixes, which require a severe pounding action.

4. Grinding and Molding

While it is still hot, a carbon-pitch mix is a heavy, doughy mass which supports its own shape but is very soft in response to any external pres-

sure. When cooled to room temperature, it becomes hard and brittle and may be ground in equipment such as that shown in Fig. 3, to a particular

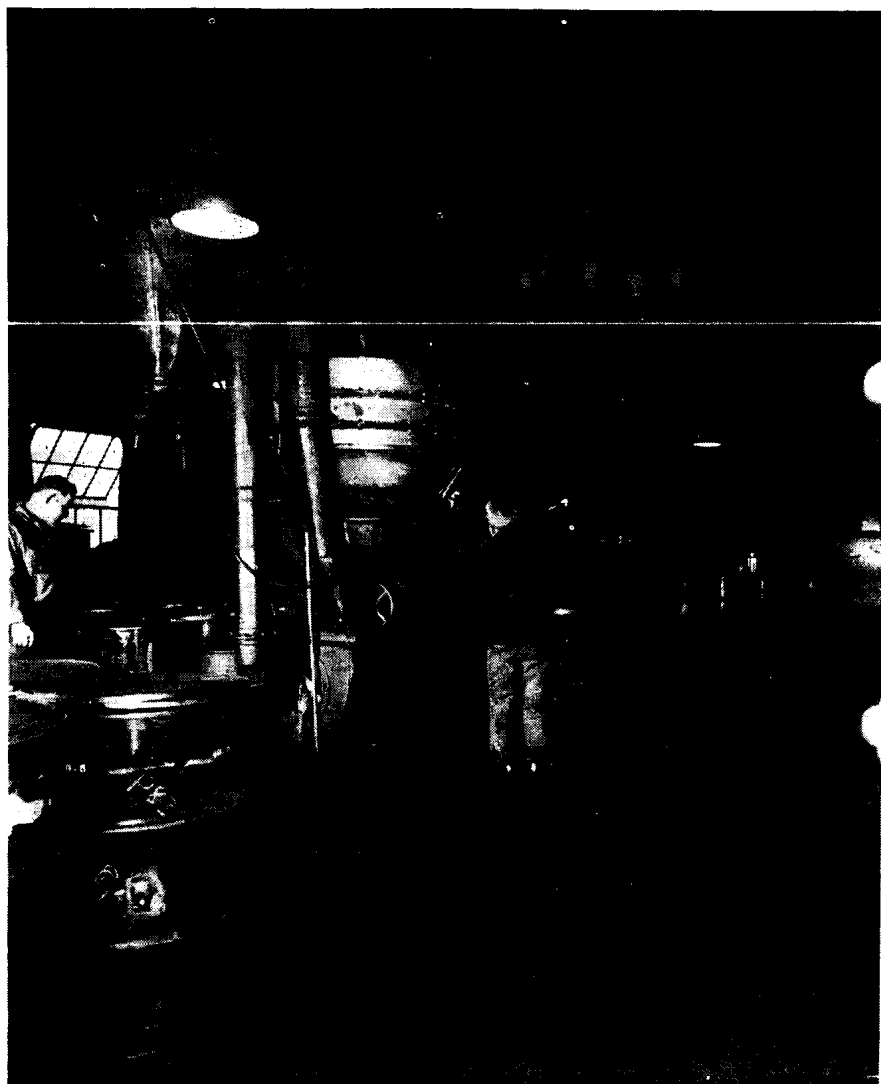


FIG. 3. Pulverizing carbon graphite mixes.

particle size for further molding. This grinding provides a material that can be molded into a piece having uniform characteristics throughout.

The molding operation may be carried out at room temperature with a resultant high porosity, or it may be done in heated molds, the mix being heated before or after it is placed in the mold. Hot molding can

result in a denser material, if desired, since it is done at a temperature at which the binder is softened.

The molding process can be carried further to include baking. The material in the mold is then heated electrically by conduction between electrodes which form two of the sides of the mold. When this is done, the major part of the carbonization of the binder occurs under pressure; as a result, a high percentage of the carbon of the binder remains in the material. The molded piece can then be baked additionally, or graphitized.

5. *Extrusion*

In extrusion, shown in Fig. 4, the hot plastic mix may be placed directly into the chamber of a press, or it may first be molded at low pressure into slugs or blocks which fit the chamber. The plasticity is ad-

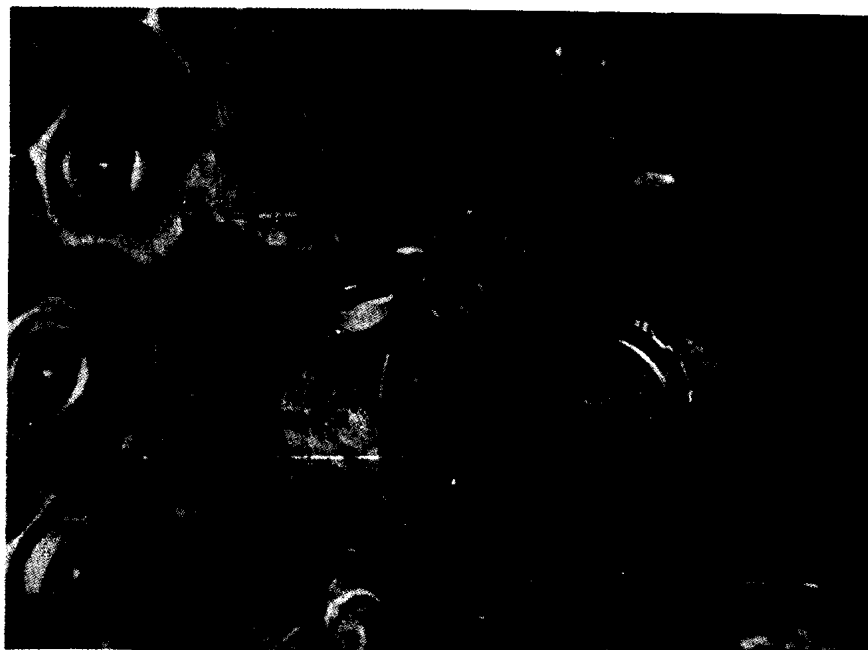


FIG. 4. Detail of extrusion operation.

justed by changing the amount of binder and the temperature so that the mix flows at the proper pressure and becomes extruded into a dense, uniform piece.

Because of the nature of flow through the extrusion die, the material acquires a structure in which any flat particles tend to line up with their

largest dimension parallel to the extrusion direction. The effect of this orientation is maintained or even exaggerated during the baking process so that in the final material the slip planes parallel to the extrusion direction still persist. The orientation effect can be minimized by choosing more isometric raw materials and by lowering the extrusion pressure.

After extrusion, sections of the material are cut at the press and cooled, and they are then ready for baking.

6. Baking

This part of the process is extremely important. During the time the temperature is rising from 125°C to 600°C , the binder is melting and then carbonizing, the material is partially plastic, the gases must be released from within the piece, and its surface must be protected from oxidation. At temperatures between 600°C and 1200°C , the heating rate may be increased because the major gas evolution has taken place and the material is now solid, but it must be protected from air with which the carbon-compound gases would react to deposit pyrolytic carbon.

The baking operation may be carried out in kilns similar to those

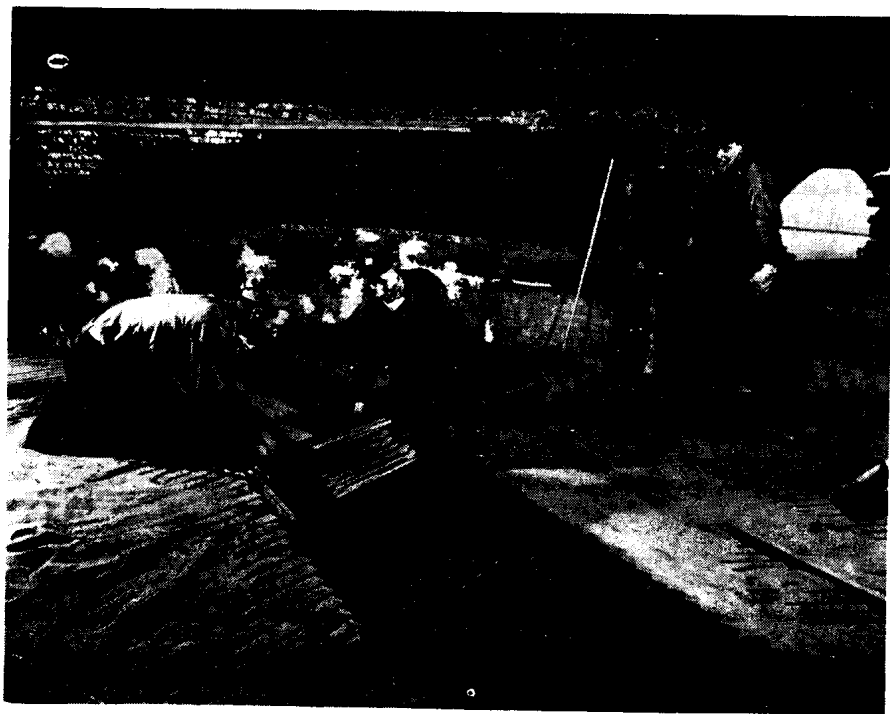


FIG. 5. Packing extruded shapes inside a baking kiln.

used in the manufacture of bricks or in special ovens designed for carbon baking. The inside of such a kiln during the baking operation is shown in Fig. 5. The material is packed in sand or coke flour to support it as it goes through the plastic temperature range. It is heated up at a rate of about 4°C per hour to 600°C , and then at a higher rate to 1200°C .

Although most of the baking of carbon is done in such kilns, some baking is done in hot molding operations, and some is now being done in continuous kilns.

Certain of the resin-type binders have made it possible to increase the baking rates considerably. The furfuryl resins are particularly useful in this respect.

7. Impregnation

Carbon from the baking process has a porosity of the order of 20%. This is too high for many uses, and it may be decreased in several ways. For low-temperature uses (chemical anodes or impervious pipe), the pores are often filled with linseed oil or with a resin, which is then cured inside the material. For high-temperature uses, the porosity may be decreased by impregnating the baked material with pitch before carrying out the graphitizing process.

The impregnation process has various modifications, among them the following. First, the material is charged into a tank which is then evacuated and heated to an appropriate temperature. Next, the liquid is permitted to flow over and around the charge, covering it completely. Then pressure is applied to force the liquid into the pores. This procedure may be employed before or after graphitization, as the application may require.

8. Graphitization

In this process the hard carbon particles change their internal crystal orientation so that the major part of the material becomes graphite. The process is carried out in either batch-type (Acheson) or continuous-type (Sanders) furnaces at temperatures between 2500° and 3000°C .

In the Acheson process, a charge of material having a volume of the order of $4 \times 4 \times 30$ feet, consisting of baked carbon pieces packed in powdered coke, is placed between two heavy electrodes and covered with an insulating blanket of coke, sawdust, and sand. Current up to 100,000 amp, at 35 to 200 volts, is passed through this charge for a period of about three days, or until about 1.7 to 2.3 kw-hr per pound of carbon has been reached. The furnace is permitted to cool for several days and is finally unpacked. The whole cycle requires about ten days.



FIG. 6. Acheson graphitizing ovens: near oven under heat; center oven being packed; far oven being unpacked.



FIG. 7. Sanders-type continuous graphitizing ovens.

Figure 6 shows three furnaces in different stages: the near one is heating up, the center one is being packed, and the far one is being unpacked.

The Sanders furnace, shown in Fig. 7, is a carbon-tube resistance furnace in which the material is passed through a trough in an electrically heated tube. The furnace tube and the electrodes are made of graphite, insulated with lampblack. Two troughs go through the hot zone, and material is passed through them in opposite directions to minimize the energy requirements. There are certain size limitations in this process, but it is more flexible for small lots of material.

9. *Pyrolytic Carbon and Graphite*

Carbon can be deposited from hydrocarbon gas at a high temperature on any inert surface which happens to be near. For example, methane mixed with nitrogen at atmospheric pressure or lower deposits carbon on available surfaces at about 1000° to 1200°C. This process has been used for many years to make deposited-carbon resistors. It is a hard, dense, gray coating with a nearly metallic luster. Recently this process has been developed to the point where, instead of carbon, graphite is deposited from the gas. This material is strongly oriented, and after annealing it comes the nearest of any artificial graphite to having the ideal crystal structure.

The processes and procedures described above are used for the manufacture of the large group of materials generically called "industrial carbon." They are used in many different combinations and permutations, to provide the necessary wide variety in material properties. A flow sheet to describe the manufacture of carbon brushes would be different from that for the manufacture of rocket nozzles, but the essentials of both processes are included in the previous information. In addition, although the basic elements of the processes have been described, many variations in production have been introduced to automate and to improve the process control. These special machines and furnaces are designed for use where production quantities justify the investment. They appear in the molding and baking of plates, in the handling of mix for large extrusion presses, in special machining operations, and in similar large-scale operations. A carbon plant can be kept as "clean" as is necessary for the specific processes, but much of it will be black.

D. PROPERTIES PECULIAR TO CARBONS AND GRAPHITES

Carbons and graphites have certain outstanding common characteristics and limitations distinguishing them from most other materials. Before the details of the differences in properties from one carbon material to another are discussed, these common characteristics should be mentioned.

Carbons and graphites do not melt at atmospheric pressure. They start to sublime appreciably at temperatures above 3000°C . They maintain their strength (in fact, they increase in strength) at temperatures up to about 2500°C , which is about 1000°C above that at which any metal maintains its strength. In this respect, carbons and graphites are similar to some of the metal carbides, nitrides, borides, and silicides. The heat conductivity of graphites is high, approaching that of the metals. Their heat capacity per unit volume is of the same order as that of the metals; and, since their density is low, the heat capacity per unit mass is high. These thermal properties make graphites important materials for service at high temperatures at which few other materials have any mechanical strength. Graphites ordinarily have low friction when rubbed against most metals; carbons have higher friction. Both carbons and graphites are brittle to macroscopic deformation, although graphites show plastic properties for microscopic deformations (hardness).

Graphites are fairly good electrical conductors; carbons can be made some one hundred times as high in resistance.

Graphites and carbons can resist most chemicals except the most strongly oxidizing acids. They oxidize in air and in oxidizing gases at higher temperatures.

Graphites and carbons can be readily machined to close tolerances. Surface finishes suitable for seal and bearing surfaces can be developed quite readily.

Carbons, when porous or in the form of powder, have the ability to adsorb large volumes of certain gases. Activated carbon and charcoal can be made with very high surface areas, and these are particularly effective in adsorbing large, complex organic molecules.

The major limitations of carbons and graphites are their brittleness and low strength with respect to metals and their oxidation in air at elevated temperatures. Their major advantages are their good mechanical and thermal properties at high temperatures, their frictional and gas adsorption properties, their machinability, their electrical properties, and, above all, the wide range of each of these properties which can be given to particular pieces by varying the choice of raw materials and the manufacturing processes.

In the next section, these and other properties will be discussed in order to show more specifically how the many property requirements called for by industrial applications of carbon products can be met by varying their final structure and composition. In Section III, these applications themselves will be studied; and finally, in Section IV, a glimpse of the future of these products will be found in the new developments which have emerged from the laboratories in the past few years to meet the demands of the space age.