CARBON: AN OLD BUT NEW MATERIAL

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This might well be called the age of materials science. The rate of our progress in such diverse fields as space exploration, atomic energy, and the conversion of heat into electrical work depends to a large extent on the development of new materials (and old materials with new properties). Many eminent scientists feel that the most important achievement in science during the last decade is the development of the transistor. This development, more than anything else, made possible the startling advances in the field of computers, which are of such importance today in our defense and technological programs. The successful development of transistors really hinged upon the development of suitable semiconductor materials—materials of ultrahigh purity and large crystal size. This was a problem in materials science!

Many of the problems in materials science today focus upon the development of materials with radically improved high-temperature properties. In space technology, the need for missiles of materials showing greater strength, thermal shock resistance, ductility, and oxidation resistance is critical. With the increasing interest in operating nuclear reactors at high temperatures to improve efficiency, a whole new materials problem has arisen—that of developing
materials that show good volume stability under high-
temperature neutron irradiation. Progress that will be
made in the efficient conversion of heat to electricity by
means of the thermoelectric effect, thermionic emission,
the fuel cell, and magnetohydrodynamics is tied insepara-
bly to advances in the development of better materials.

With the need for development of more and better mate-
rials becoming increasingly apparent, there has been a
great upswing in materials science research in many labora-
tories. In addition, universities are accelerating the training
of graduate students in materials science. Studies are in
progress on the preparation and examination of materials
consisting of individual elements or combinations of ele-
ments from most of the periodic table. One element re-
ceiving much new research attention today is carbon. This
is not surprising, even though carbon materials have been
known and used extensively for many years. Carbon has
one of the lowest vapor pressures of any element; it sub-
limes at atmospheric pressure around $3,350^{\circ}C$\textsuperscript{11} and melts
around $3,700^{\circ}$. At temperatures above $2,000^{\circ}$, carbon has
unusually good thermal and mechanical properties. Bodies
and shapes made from carbon are comparatively easy to
fabricate. Furthermore, carbon is in abundant supply and
hence relatively cheap.

*Crystal Structure of Graphite*

Carbon exists in two crystalline forms, diamond and
graphite. In an early application of X-ray diffraction it was
shown that, in diamond, each carbon atom is covalently
bonded to four other carbon atoms arranged tetrahe-
drally.\textsuperscript{12} The carbon-carbon bond distance is $1.54\,\text{Å}$. The
extreme hardness of diamond is the direct result of such a
configuration, since rupture of this isotropic structure
would require the breaking of many strong bonds. Dia-
mond has no utility at atmospheric pressure at temperatures above 1,500°C, because of its rapid transformation to graphite.\textsuperscript{121} Diamond, of course, has many important uses at low and moderate temperatures.

The recent successful growth of synthetic diamonds from graphite at pressures of about 85,000 atm. and at temperatures of about 1,600°C \textsuperscript{141} makes, in itself, an epic story in materials science. Possibly a bigger story is now in the process of being told—that is, the production of diamonds that have semiconducting properties.\textsuperscript{151} Diamond will not be considered further in this article.

\textit{Ideal graphite structure.} Bernal \textsuperscript{141} in 1924 proposed the now accepted stable hexagonal lattice, which is illustrated in Figure 99, as the structure of ideal graphite. The structure is composed of a system of infinite layers of fused hexagons. Within each layer, the carbon-carbon bond distance is 1.415 Å, a spacing indicative of one-third double-bond character.\textsuperscript{171} Each carbon atom has four valence electrons. Three of these electrons (usually called σ electrons) are engaged in forming regular covalent bonds with neighboring carbon atoms. These electrons are localized as are the electrons in diamond. The fourth electron (usually called a π electron) resonates between many valence-bond structures, effectively giving each carbon-carbon bond a one-third double-bond character.

The individual layers are held parallel at a separation of 3.3538 Å \textdegree{}13°C by weak van der Waals’-type forces. This spacing has been carefully measured by X-ray diffraction \textsuperscript{81} and closely confirmed \textsuperscript{161} on crystalline, natural graphite from Ceylon. In precise work it is necessary to quote the temperature at which the interlayer spacing is given because of the large coefficient of thermal expansion of graphite perpendicular to the layer planes.\textsuperscript{81, 161} The thermal expansion of graphite parallel to the layer planes is very small.\textsuperscript{151}
The structure shown in Figure 39 is the so-called hexagonal form of graphite. The carbon layers form a stacking sequence \textit{ababab}, where one-half of the carbon atoms in any one layer lie above the center of the hexagons in the layer immediately below. In alternate layers, the carbon atoms are directly imposed over each other. Although this is the predominant layer stacking in graphite, in some cases a fraction of rhombohedral structure having a stacking sequence \textit{abcabcabc} is found.\textsuperscript{111} This structure was proposed in 1942 to account for additional reflections found in X-ray diffraction studies on natural graphites. It is metastable with respect to the hexagonal form, from which it may be produced by fine grinding \textsuperscript{121} and to which it reverts by heating to around 1,300°C.
Deviations from the ideal graphite structure. Deviation among most carbons of commercial interest is the rule rather than the exception. The most important deviation is the presence of stacking disorders between the layer planes in carbon. Pioneering studies of Franklin [13] and Bacon [14] have shown that, in different carbons, the fraction of stacking disorders can vary from one to essentially zero (that is, ideal graphite). In the case of a stacking disorder, adjacent layer planes, while still parallel, are randomly rotated so that there is no longer a fixed relation between the location of the carbon atoms in the two planes. Variations in the fraction of stacking disorder (\( \rho \)) are accompanied by variations in the measured spacing between layer planes, as shown in Figure 40. The measured interlayer spacing increases from 3.354 Å (ideal graphite) to 3.440 Å for a carbon having complete stacking disorder. The latter material is now called turbostratic carbon. [12] According to Bacon, there are four different spacings that can exist in a stack of carbon layer planes: (1) between two oriented layers, 3.354 Å; (2) between two disoriented layers each of which has a disoriented layer on each side of it, 3.440 Å; (3) between two disoriented layers, one of which is followed by an oriented layer, 3.408 Å; and (4) between two disoriented layers each of which is followed by an oriented layer, 3.376 Å. The spacings in Figure 40 are those that would be measured from X-ray diffraction patterns of carbons (see below) and are a result of the presence of varying amounts of the four spacings proposed by Bacon.

The presence of stacking disorders between the layer planes of carbon is a result of the fact that the layers have a finite size. That is, carbon is composed of crystallites having a range of both heights (a varying number of layer planes per crystallite) and layer diameters. The average crystallite size in carbons varies widely—all the way from a low of 10 Å for some carbon blacks and activated carbons to a high
of 10^8 Å for some natural and special synthetic graphites. It is suggested \cite{10} that the ordering of layers in a crystallite first commences (that is, \( p \) becomes <1.0) when the crystallite diameter reaches about 150 Å. Valence bonds between neighboring crystallites tend to stabilize the layers in rotated positions, while the attractive forces between the

**Fig. 40.** Variation in the fraction of stacking disorder with mean interlayer spacing.\cite{13}
layers tend to align them. The latter force increases as the square of the diameter and evidently becomes the determining factor for crystallite diameters above 150 Å. The major decrease in the fraction of displaced layers occurs up to an average crystallite diameter of about 2,000 Å. At this diameter \( p = 0.05 \).\(^{141}\)

Other deviations from the ideal graphite structure can be considered briefly. Carbons of small crystallite size frequently have a fraction of disorganized material present. This material consists, in part, of aliphatic groups attached to the edges of layer planes. The material can be responsible for the cross-linking between crystallites.

Well-known solid-state defects like twin lines,\(^{172}\) edge dislocations,\(^{181}\) screw dislocations,\(^{199}\) and vacancies\(^{209}\) have been reported in graphite. Dislocations are observed by transmission electron microscopy on ultrathin sections of graphite. Vacancies are produced in appreciable concentrations when graphite is irradiated with neutrons or other high-energy particles, which cause displacement of carbon atoms from their normal sites within a layer plane. The displaced atoms usually reside in interstitial sites between the layer planes. Vacancies in natural graphite have also been produced by rapidly quenching it from temperatures around 2,500°.\(^{211}\) The quenched graphite was unusually reactive to oxidizing gases, with substantial pitting observed in the layer plane. It thus appears that carbon atoms surrounding a vacancy are highly reactive.

*Electrical and Thermal Properties of Graphite Single Crystals*

As expected from the pronounced difference in bonding within the layers of carbon as compared to that between the layers, the thermal and electrical properties of carbon are highly anisotropic. Much has been published on these
properties, both experimental and theoretical, and it is not the purpose here to consider this material in any detail; good general reviews are available.\textsuperscript{[22, 23]} Values of the electrical resistivity and thermal conductivity of graphite single crystals will be considered briefly, since they will serve as reference limits when considering the properties of multi-crystalline carbons.

The anisotropy of the electrical resistivity of graphite single crystals exceeds that of any other property. This is clear from the experimental values available, even though there is some disagreement on the extent of the anisotropy because of differences in the crystal perfection of specimens examined. In the direction parallel to the layer plane, there is reasonable agreement that the room temperature resistivity is about $4 \times 10^{-3}$ ohm cm.\textsuperscript{[24]} Perpendicular to the layer planes, resistivity values vary from around 1 ohm cm \textsuperscript{[25]} to $4 \times 10^{-3}$ ohm cm.\textsuperscript{[24]} Thus the ratio of electrical resistivities is at least 100.

Measurements of thermal conductivities on small graphite crystals are difficult. Nevertheless there appears to be agreement, from the limited data available, that the room temperature values are about 4.0 and 0.8 watts/cm$^\circ$C, respectively, in the directions parallel to and perpendicular to the layer planes.\textsuperscript{[22]} Thus the ratio of thermal conductivities is about 5.

\textit{The Preparation of Carbons and Some of Their Interesting Properties}

Carbons of widely different properties (properties approaching those of ideal graphite more or less closely) can be prepared by starting with different carbonaceous materials (in the form of solids, liquids, and gases) and treating them in various ways. The variation in properties is a result primarily of a variation in carbon crystallite size and
orientation. The preparation and properties of both "old" and "new" carbon materials can now be considered.

**Bulk baked and graphitized carbon bodies.** The carbon body that is familiar to us today appears to have had its beginning in 1800 when Sir Humphry Davy first employed carbon electrodes to produce an electric arc. His electrodes were simply rods cut from carbonized wood. During most of the nineteenth century the majority of the development work in the carbon industry was directed toward producing improved electrodes for arc lighting. In the decade 1890-1900, there came a succession of inventions and developments in the electrothermal and electrolytic field, all of which required baked or graphitized carbon bodies. In 1896 Castner [26] and Acheson [27] found that some turbostratic carbons could be converted into graphite materials by heating to sufficiently high temperatures—2,500° and above. This marked the beginning of a new era in which the carbon industry expanded and developed improved baked and graphitized carbons for use primarily in (1) electrolytic manufacture—e.g. of alcalies, chlorine, aluminum, and magnesium; (2) electrothermic production—e.g. of calcium carbide and silicon carbide; and (3) electric furnaces—e.g. for steel, copper, ferroalloys, and phosphorus. Then, in 1942, when Fermi and a group of scientists produced a self-sustaining nuclear chain reaction, they used graphite as the moderator in their reactor. This opened up a whole new outlet for graphite and at the same time produced materials problems on which research and development studies are still in progress.

**Method of production of carbon bodies.** Bulk carbon is basically a composite mixture of carbon particles (called the filler) and a suitable binder. The most common filler is petroleum coke, which today is obtained largely by the cracking of heavy refining oil that produces gasoline, other light fractions, and coke. Usually the binder is coal tar
pitch, the heavy residue derived from the distillation of coal tar from by-product coke ovens. The petroleum coke, as received from the oil industry, is first heated in the absence of air (calcined) to about 1,500° to reduce its volatile matter content and to preshrink the coke. Excessive shrinkage of the coke during the baking of the carbon body produces undesirable cracking. The calcined coke (about 100 parts by weight) is ground to the appropriate particle size and mixed thoroughly with melted pitch (about 30 parts by weight) at about 150°. The mix is then formed into the desired shape by extrusion or molding. The formed body is baked, in the absence of air, to about 1,000°. The function of the baking operation is to convert the pitch from a thermoplastic material to an infusible solid. As the binder is pyrolyzed, large quantities of hydrogen and hydrocarbons are evolved, resulting in the loss of about 40% of the binder weight. Thus, the baked body is composed of about 85% (by weight) of filler carbon and 15% binder carbon.

As we shall see later, the open porosity of baked carbons is typically between 25 and 30%. For some end uses, a material of much lower porosity is necessary. The most common method used to decrease the porosity of a carbon body is to impregnate it with a fluid (frequently a coal tar) which, upon subsequent pyrolysis, deposits secondary carbon in the open voids. A body may be impregnated a number of times, with the impregnant usually being coked after each impregnation.

The gas-baked carbon body is composed of small carbon crystallites. Within these crystallites, the layer planes are all randomly rotated. When the baked body is heated in the absence of air to temperatures between 2,500 and 3,000°, the carbon crystallites grow sufficiently to impart substantial stacking order between the carbon layers. The results of “graphitization” include a substantial change in the electrical, thermal, and mechanical properties of the
carbon body. In addition, a body of much higher purity is produced because of the liberation of additional hydrogen, sulfur, and metallic impurities. In some cases the liberation of metallic impurities is enhanced by graphitizing in a halogen atmosphere.

Mechanism of carbonization and graphitization. The carbonization and graphitization of the filler and binder phases will first be considered separately, and then the effect of interaction of the two phases will be discussed. Consider petroleum coke (the filler) first. When heavy petroleum residues are heated between about 350 and 550°, they crack, liberating low-molecular weight gases and forming a solid phase—“green” petroleum coke. Petroleum cokes show remarkable flow patterns within the particles, caused apparently by the evolution of gases and aided by the thermal motion of the viscous mass during coking. It is found [28] that large, platelike aromatic molecules are aligned parallel to the flow as a result of shear stresses. During calcination the aligned structure is preserved (see Fig. 41), although fissures develop and enlarge as additional volatile hydrocarbons are evolved. Calcined petroleum coke is a turbostratic carbon, containing crystallites of about 30 Å in diameter. Upon heating above the calcination temperature, crystallites grow slowly up to about 2,000° and then grow rapidly. The extent of crystallite growth under given heat treatment conditions is markedly sensitive to the extent of platelet alignment in the green coke. The better and more extensive this alignment, the greater is crystallite growth. This fact is taken to indicate that vapor-phase condensation is not the likely mechanism of graphitization, since such a process should be nearly independent of coke structure. The mechanism favored [29] for crystallite growth involves the displacement and rearrangement of crystallites relative to each other. The more nearly two crystallites are aligned with their layers parallel
to each other, the easier it is for them to become sufficiently rearranged by thermal motion to coalesce. This leads to crystallite growth without mass transfer or the work of breaking strong chemical bonds. As will be seen later in a striking example, low-temperature carbons which have

![Image: Texture of a typical calcined petroleum coke: × 75.]

their crystallites poorly aligned or strongly cross-linked undergo negligible additional growth, even when heated to 3,000°.

It has been found that the extent of platelet alignment in green petroleum coke is dependent upon at least two fac-
tors: (1) the manner of coking and (2) the cleanliness of the charging stock. To attain good alignment, the liquid hydrocarbons should be in a state of substantial quiescence and thermal homogeneity during solidification. The presence of granular precipitates or asphaltenes in the oil during coking is found to increase markedly the rate of coking and to prevent good alignment of adjacent platelike molecules.

Consider now the carbonization and graphitization of coal tar pitch (the binder). A typical pitch contains about 90% by weight of aromatic molecules with platelet diameters from 4 to 8 Å. Upon heating the pitch to between about 450 and 550°, these molecules lose hydrogen and low molecular weight hydrocarbons and condense into platelets of larger size, resulting in the formation of a solid, "green" pitch coke. The extent of crystallite growth upon subsequent heat treatment to graphitization temperatures depends, as is the case with petroleum coke, upon the perfection of crystallite alignment in the green coke. This alignment, in turn, is at least dependent upon (1) the nature of the aromatic compounds in the pitch and (2) the character of the insoluble phase present. Considering the first point, pitch is estimated to contain about 5,000 different compounds. These compounds would be expected to yield cokes showing wide differences in their graphitizability. For example, the crystallite growth of cokes produced from anthracene and phenanthrene, two compounds identified in pitch, has been studied. These compounds, having the same formula (C_{14}H_{16}), are isomers. Upon heat treatment of the cokes to 3,000°, the anthracene- and phenanthrene-derived carbons had average crystallite diameters of about 2,000 Å and 200 Å respectively. Considering the second point, pitches are known to contain varying amounts of insoluble particles. Removal of the particles (in the pitch because of entrainment of solids from the
coke oven) substantially enhanced crystallite alignment in the coke subsequently produced.\textsuperscript{[54]} It is concluded that these particles act as nuclei for the coking of aromatic compounds in the pitch and decrease crystallite alignment because of their large surface heterogeneity (the relation between crystallite alignment and surface heterogeneity will be discussed shortly).

There is much concern about the relative extents of crystallite growth of the filler and binder within a carbon body upon graphitization. Some pitches, when heat-treated alone, graphitize as well as petroleum coke.\textsuperscript{[56]} However, Noda and Inagaki\textsuperscript{[56]} conclude that pitch is less graphitizable when it is heat treated with an admixture of petroleum coke than when heat treated alone. They found that graphitized pitch carbon in a body had an interlayer spacing of 3.38 Å and a crystallite height of 260 Å. By comparison, the pitch carbon graphitized alone had an interlayer spacing of 3.36 Å and a crystallite height of 340 Å. They concluded that, in a carbon body, pitch exists in a thin film around the filler particles. As such, it has difficulty flowing even when it softens and, consequently, the platelet groups have difficulty orienting.

Some significant work on the kinetics of graphitization of a baked carbon body between 2,000 and 3,000\textdegree\ carbon has been conducted.\textsuperscript{[57]} Samples were rapidly plunged into the high-temperature zone of a furnace (containing argon) and held for varying lengths of time. Interlayer spacings were then accurately measured on the samples. The results are shown in Figure 42. One can see that at each graphitization temperature the interlayer spacing decreases rapidly at first, and then more and more slowly, as it approaches (practically speaking) some limiting value. These kinetics are consistent with there being a steady increase in activation energy for additional crystallite growth with increase in extent of graphitization. Much additional kinetic work
needs to be done, not only on the effect of soak time, but also on the effects of heating and cooling rates upon graphitization and upon the resulting electrical, thermal, and mechanical properties of carbon bodies.

![Graph showing interlayer spacing](image)

Fig. 42. Studies of kinetics of graphitization of a typical carbon body.$^{[37]}$

It is of interest to consider the extent to which complete three-dimensional ordering has been achieved upon the graphitization of carbon bodies. The interlayer spacing of four different carbon bodies has been accurately measured,$^{[9]}$ after heat treatment to $3,600^\circ$ under 10 atm of argon pressure. The lowest spacing found was $3.3569 \text{ Å}$ ($15^\circ\text{C}$), corresponding to a fraction of displaced layers of 0.10. Bacon$^{[44]}$ very carefully studied the extent of crystalline perfection of three artificial graphites. The sample of greatest perfection, which had a fraction of displaced layers of only 0.019, is thought to have reached a temperature of $3,200^\circ$ and to have been produced from a coke of unusually
good crystallite alignment. Its X-ray diffraction pattern, shown in Figure 43, reveals an unusually large number of diffraction peaks.

![X-ray diffraction pattern](image)

**Fig. 43.** X-ray diffraction pattern (Cu-Kα radiation) of a highly graphitized artificial graphite.\(^{[44]}\)

**Physical structure of carbon bodies.** The density of ideal graphite is 2.268 g/cc, but in practice the density of carbon bodies is considerably less than this figure because of porosity between filler particles and between crystallites within both the filler and binder carbon. Figure 44 is a micrograph of a longitudinal section of a 10-inch diameter graphitized electrode.\(^{[58]}\) The apparent density of this body is 1.60 g/cc, and its total porosity is about 29%. The voids between filler particles and fissures within filler particles are clearly seen. Figure 45 is a transmission electron micrograph of a thin section cut from nuclear graphite.\(^{[20]}\) This micrograph shows a strong resemblance to the familiar grain structure of etched metal specimens. Individual crystallites can be recognized; they have an average layer diameter of about 3,000 Å. Porosity between crystallites is clearly in evidence. Area \(A\) is a pore at the junction of three crystallites. Line \(MN\) is a sharp boundary of about 50 Å width between two crystallites.

As shown,\(^{[40]}\) some of the porosity between carbon crys-
tallites is unavailable to helium at room temperature. This
is taken to mean that it is blocked off behind openings less
than about 2.8 A in diameter. The amount of pore volume
closed to helium in a variety of calcined petroleum cokes
has been measured, along with the relative extent of crys-
tallite alignment from the intensity of the (002) X-ray dif-
fraction peak. It was found that the amount of closed-pore
volume increases with a decrease in the extent of crystallite
alignment, as shown in Figure 46. The effect of crystallite
size on the amount of pore volume closed to helium in se-
lected carbon bodies has also been investigated. It was
found that, as the crystallite size decreases, the fraction of
pore volume inaccessible to helium increases. It was con-
cluded that the closed-pore volume is coextensive with the
crystallite surfaces and is the result of small separations be-
tween adjoining crystallites. Walker and Geller measured the pore volume closed to helium in a graphitized
petroleum coke and in a graphitized carbon body contain-
ing the same petroleum coke of identical particle size. They
found, by difference, that the amount of closed-pore volume
per unit weight of binder carbon considerably exceeded
that in the filler carbon. On the basis of previous results,
this also suggests that the crystallite size in the binder car-
bon is less than that in the filler carbon.

The open porosity in carbon bodies has been studied by
gas adsorption and mercury porosimetry. The pore
volume distribution in voids greater than 400 A in radius
(usually called the macropore volume) for samples of un-
impregnated and impregnated nuclear graphite is shown
in Figure 47. For the unimpregnated body, the majority of
this porosity is usually located within a fairly narrow range
of pore sizes. This volume is created by the packing of filler
particles. As is seen, impregnation primarily reduces this
volume. After seven impregnations the open pore volume
of this nuclear graphite was reduced from 22 to 7%. By as-
suming cylindrical pores, the expression \( A = 2V/\bar{r} \) can be used to calculate the total surface area in the macropore range. That is, for each volume increment (for example, between data points in Fig. 47) a corresponding surface area increment, \( A \), can be calculated by taking the arithmetic average pore radius, \( \bar{r} \), over the increment. If this is done, it is frequently found that the calculated macropore

Fig. 44. Photomicrograph of a longitudinal section of a graphitized electrode; \( \times 10^{10} \).
surface area is greater than the total surface area as measured by gas adsorption. A reasonable explanation is that the macropores contain pore constrictions, with the result that too high a volume of mercury is assigned to too small a pore size.

The specific surface area of baked and graphitized carbon bodies, as calculated from low temperature (78°K)

**Fig. 45.** Transmission electron micrograph of a thin section of nuclear graphite: \( \times 170,000 \).
nitrogen gas adsorption, is usually low—in the range from 0.5 to 2.0 m²/g. This area can be compared with the area calculated from crystallite size data. For example, a baked carbon body with an average crystallite size of 30 Å would have a crystallite surface area of about 900 m²/g. The great difference between the measured and calculated surface areas means that essentially all the crystallite surfaces are inaccessible to nitrogen at 78°K. This is a result of a high

![Graph](image)

**Fig. 46.** Variation of closed-pore volume in calcined petroleum cokes with crystallite orientation.\(^{[16]}\)
degree of crystallite alignment and a close approach of crystallites in regular carbon bodies. It will be seen later that this is not always the case with carbons.

![Graph](image)

Fig. 47. Typical distribution of open-pore volume in nuclear graphites of different porosities.\(^{44}\)

From experiences with coal, there was concern that the surface areas of nuclear graphite as measured by low-temperature gas adsorption might be low because of activated diffusion.\(^{48}\) That is, the adsorbate might be able to penetrate only a small fraction of the pore area in the time allotted for equilibration. Therefore, areas obtained from low-temperature adsorption were compared with those obtained from adsorption of argon at room temperature. Previous work had shown that gas diffusion and equilibration of argon is rapid even in molecular sieve materials at room temperature. The agreement in the areas was excellent, thereby confirming the conclusion that nuclear graphite does have a low, open surface area.

**Electrical and thermal properties of carbon bodies.** We will consider briefly the electrical resistivity and thermal
conductivity of carbon bodies. Petroleum cokes are irregular in shape and, upon formation of carbon bodies containing them as filler, the particles tend to align with their longer axes either parallel to the extrusion direction or perpendicular to the molding direction. The degree of alignment increases as the particles become more asymmetric in shape. Also, carbon crystallites which compose a coke particle are aligned with their layer planes more or less parallel to the longer axes of the particle.\textsuperscript{1231} Thus, because of the marked anisotropy of such properties as electrical resistivity and thermal conductivity within a carbon crystallite, particle alignment imparts to formed carbon bodies some degree of anisotropy in these properties. As will be seen, however, the extent of anisotropy is much smaller than that found in graphite single crystals. The primary reason for this is that much of the resistance to electron and heat flow in a carbon body is contributed, not by the filler particles, but by the binder-carbon bridges between filler particles.\textsuperscript{1461} This is a result both of the higher resistivity of the binder coke to electron and heat flow and of a decrease in area for flow at the binder constrictions.

Typical room-temperature values of electrical resistivity and thermal conductivity parallel to the extrusion direction in baked carbon bodies (total porosity of about 25\%) are \(5 \times 10^{-3}\) ohm cm and \(4 \times 10^{-2}\) watt/cm/°C respectively. Upon graphitization at about 2,800°C, a carbon body of similar porosity has typical electrical resistivities of \(7 \times 10^{-4}\) and \(9 \times 10^{-4}\) ohm cm parallel and perpendicular to the extrusion direction respectively. The anisotropy of electrical resistivity is only 1.3 compared to at least 100 in a single crystal. Comparable graphitized carbon bodies have typical thermal conductivities of 2.3 and 1.4 watts/cm/°C parallel and perpendicular to the extrusion direction respectively. The anisotropy of thermal conductivity is 1.6 compared to about 5 for a single crystal.
Carbon Black

History and methods of preparation. Carbon blacks are formed by the thermal decomposition of gaseous and liquid hydrocarbons, with the operation occurring at essentially atmospheric pressure. Two methods are used to produce the majority of the carbon black manufactured today: the channel process and the furnace combustion process. In both of these the heat required for decomposition of the hydrocarbons is supplied by their partial combustion.

The channel process has evolved since its beginning in 1872. Carbon black is collected by impingement of small, natural gas diffusion flames on relatively cool channel iron surfaces. The character of the black, particularly its particle size, can be varied by altering the size of the burner tip used and the distance from the burner tip to the channel surface. The narrower the slot in the tip, the finer the particle size of the black produced. At an optimum distance between the channel and the burner tip, both the particle size and black concentration are at a maximum. If the distance is increased, the particle size and yield of the black are reduced because of its reaction with oxygen. This reaction is deliberately encouraged in some cases in order to yield smaller blacks of higher porosity and oxygen content.

Until 1940 the channel black process was used to produce the majority of carbon black consumed, but since then the furnace combustion process has increased rapidly and today is responsible for the greater amount of black. This is apparently a result of easier processing of furnace blacks in synthetic rubber. Furnace combustion blacks are also produced in diffusion flames. However, instead of the large number of tiny flames utilized in the channel process, a large volume of natural gas and/or liquid hydrocarbons and air undergoes combustion and cracking in firebrick-
lined furnaces. The carbon black, suspended in the spent reaction gases, is collected by a combination of electrostatic precipitation and centrifugal force. This process is capable of producing blacks of considerably larger particle size than is the channel process.

A small but important class of carbon blacks is produced in the furnace thermal process in which the black can be formed in the absence of oxygen or oxygen-containing product gases. When natural gas is used, carbon black is produced in an intermittent operation. Air and natural gas for complete combustion are first fired into an insulated furnace, heating it to as high as 1,400°C. The natural gas is then forced through the furnace and cracked, producing a very coarse carbon black. The particle size of the black can be reduced somewhat by diluting the natural gas with an appropriate amount of flue gas from the heating cycle. Furnace thermal black is also produced by the continuous decomposition of acetylene. Since this reaction is exothermic, the heat liberated from the decomposition can be used to maintain the reaction.

About 90% of the carbon black produced is used as a filler in rubber. The carbon increases the strength and resistance to abrasion of rubber. Carbon black is also used as an additive to inks, paints, and plastics, and as thermal insulation.

Mechanism of carbon black formation. There are, broadly speaking, two main views on carbon formation in flames: (1) hydrocarbons decompose into acetylene and other low-molecular weight species, followed by a process of simultaneous condensation and dehydrogenation to produce carbon; and (2) hydrocarbons, by a process of dehydrogenation and condensation, produce polymers of high molecular weight (carbon). Porter contended that the first mechanism, through acetylene as the intermediate, accounts for most of the production of carbon in diffusion flames.
He reasons on the basis of kinetic and thermodynamic arguments that, at temperatures above 1,000°C, decomposition predominates over polymerization. Therefore, if carbon is to be produced by mechanism (2), the hydrocarbons would have to remain in the preheating zone of a flame long enough (at temperatures below 1,000°C) to produce a polymer that would be stable above 1,000°C. This polymer could then dehydrogenate and produce carbon. However, Porter concludes that the hydrocarbons in a diffusion flame are usually heated to 1,000°C too rapidly to allow polymers of sufficient size to grow. Although these arguments are plausible, it cannot yet be considered that the mechanism of carbon formation is well understood.

Structure of carbon blacks. Electron microscope studies have revealed that the particles of most carbon blacks are essentially spherical in shape. There is a great range of average particle diameters in carbon blacks—from a low of about 100 Å for the smallest channel black to a high of about 5,000 Å for the coarsest furnace thermal black. Carbon blacks are composed of varying fractions of turbostratic crystallites and disorganized carbon. The size of the crystallites is essentially independent of the black particle size; the crystallite size in almost all cases is in the range from 10 to 20 Å. The amount of disorganized carbon is as high as 20% of the total carbon present in the smallest particle-sized channel blacks. Carbon blacks are more or less porous, depending upon the perfection of their crystallite alignment, the amount of disorganized carbon present, and the extent of their oxidation during preparation. A method based on low-temperature adsorption data and helium densities, which gives information on the nature of the porosity within blacks, recently has been presented. These data are summarized in Table 12 for a very fine-sized channel black and a widely used oil-furnace combustion black. It is seen that the channel black has considerable internal poros-
ity, whereas the internal porosity in the oil-furnace combustion black is negligible. The amount and nature of the porosity in blacks is important in affecting the behavior of the black in its applications.

**Table 12. Physical Data for Two Selected Carbon Blacks**

<table>
<thead>
<tr>
<th>Property</th>
<th>Channel Black</th>
<th>Furnace Combustion Black</th>
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<tbody>
<tr>
<td>Helium density, g/cc</td>
<td>2.02</td>
<td>2.05</td>
</tr>
<tr>
<td>Open-pore volume, cc/g</td>
<td>0.170</td>
<td>0.092</td>
</tr>
<tr>
<td>Apparent density, g/cc</td>
<td>1.50</td>
<td>2.05</td>
</tr>
<tr>
<td>Total surface area, m²/g</td>
<td>1,000</td>
<td>69</td>
</tr>
<tr>
<td>Free surface area, m²/g</td>
<td>587</td>
<td>55</td>
</tr>
<tr>
<td>Internal surface area, m²/g</td>
<td>413</td>
<td>4</td>
</tr>
<tr>
<td>Electron microscope surface area, m²/g</td>
<td>264</td>
<td>74</td>
</tr>
<tr>
<td>Average pore diameter, Å</td>
<td>17</td>
<td>20</td>
</tr>
</tbody>
</table>

**Graphitization of carbon blacks.** The heat treatment of carbon blacks to temperatures between 2,000 and 3,000°C produces interesting results. Bischof and Warren,\(^{126}\) using X-ray diffraction, performed pioneering studies on the graphitization of Spheron-6, a channel black having an arithmetic mean particle diameter of about 250 Å. They found that, upon heat treatment to 2,800°, the crystallite diameter and height were increased only to about 65 and 40 Å respectively. The graphitized black had an interlayer spacing of 3.44 Å, indicating no stacking order. It is shown \(^{126}\) that the extent to which the crystallites in carbon black grow upon heat treatment is limited by the particle size of the black. Figure 48 shows results for the growth in crystallite diameter with temperature of three blacks of widely different particle diameters. It is suggested that crystallites in carbon blacks never grow to a size greater than one-third of the particle diameter.\(^{116}\)

The heat treatment of carbon blacks has been studied by
CARBON: AN OLD BUT NEW MATERIAL

electron microscopy.\cite{28, 51} Figure 49 shows a large furnace thermal black both in the raw state and after heating to 3,000°. No appreciable change in the appearance of the

![Crystallite Diameter vs Temperature Graph]

Fig. 48. Crystallite growth of carbon blacks upon heat treatment to elevated temperatures.\cite{50}

black is observed for heat treatment up to 1,500°. As the heat-treatment temperature is further raised, dark strips, which run from the periphery to the inside of the particle, are noted. Above 2,500° the dark strips grow into trigonal
Fig. 49. Electron micrographs of (A) raw furnace thermal black and (B) black heated to 3,000°C; × 35,000. [201]
or trapezoidal dark shapes, whose bases coincide with the edges of the polygonal outlines of the particle. It is reasoned that these dark areas are produced by diffraction effects from the layer planes of the crystallites. This leads to the conclusion that crystallites are in preferred orientation, with their layer planes forming the particle surface. Figure 50 presents a schematic diagram of alignment of the crystallites in a raw and heat-treated carbon black.\(^{(29)}\) As discussed previously, the extent of crystallite alignment in the raw carbon blacks varies widely, resulting in a variation in the extent of open, internal porosity.

![Diagram A and B](image)

**Fig. 50.** Schematic diagram of alignment of crystallites in (A) raw and (B) heat-treated carbon black.\(^{(29)}\)

**Effect of graphitization of carbon blacks on their physical structure and surface properties.** The degree of change in the surface area of carbon blacks upon heat treatment depends upon the amount of internal surface area in the raw black. Blacks with large internal surface areas undergo large decreases in area, whereas, blacks with negligible internal area undergo negligible decreases in area. The area decrease is caused by the removal of open, internal porosity. Upon heat treatment of the channel black in Table 12 to 2,800°C, its surface area decreased from 1,000 to 251 m²/g.
—or very close to its geometric area. On the other hand, the nonporous furnace combustion black in Table 12 underwent a negligible change in surface area upon heat treatment to 2,800° —from 69 to 68 m²/g. Figure 51 shows the change in surface area of a medium channel black upon heat treatment. The initial increase in area is produced by activating the black, upon removal of its volatile matter as oxides of carbon. Above 1,000°, the area of the black decreases sharply.
Despite the removal of open porosity from carbon blacks upon heat treatment, the helium densities of the blacks frequently undergo large decreases. For example the helium density of the channel black in Table 12 decreases from 2.02 to 1.52 g/cc upon heat treatment to 2,800°. It is shown that the extent of the change in helium density upon heat treatment can be affected by preoxidation of the black. The channel black Spheron-6, with negligible internal porosity, undergoes a change in helium density from 1.94 to 1.92 g/cc upon heat treatment at 2,500°. Preoxidation of the black to 22% weight loss results in a decrease in helium density from 1.95 to 1.64 g/cc upon heat treatment to 2,500°. By contrast, oxidation of the heat-treated (raw, original) black to 22% weight loss increases the helium density to 1.98 g/cc.

Heat-treated carbon blacks have been studied very extensively by surface chemists, because of their large and homogeneous surface. That is, the surface consists ideally of only the layer planes of carbon. The extent of surface homogeneity has been determined in three main ways: (1) from the appearance of an entire adsorption isotherm, (2) from heats of physical adsorption as a function of surface coverage with adsorbate, and (3) from a deviation of an adsorption isotherm from linearity at very low coverages.

To consider the first method, it has been predicted theoretically that multilayer adsorption on a homogeneous surface should give rise to an isotherm composed of a number of steps. A step should appear at the completion of each adsorption layer. The adsorption of argon at 78°K on a thermal black, similar to that shown in Figure 49, has been measured after its heat treatment at a series of temperatures. The development of steps of increasing steepness in the isotherms with increasing heat-treatment temperature is seen in Figure 52, indicating a progressive increase in surface homogeneity. The steepness of the steps in the
isotherm for the black heated to 2,700°C appears to be comparable with that found in the isotherm obtained from the adsorption of argon on Ceylon graphite heated to 2,700°C.\[^{[36]}\]

Fig. 52. Change in surface homogeneity of carbon black upon heat treatment as followed by adsorption isotherms.\[^{[37]}\]

To consider the second method, the change in the heat of physical adsorption with coverage is dependent upon the degree of homogeneity of the surface. If the surface is heterogeneous, physical adsorption occurs on the strong sites first, and a large decrease in heat of adsorption with increase in coverage results. For a very homogeneous surface there is little change of heat of adsorption with coverage until significant adsorbate interaction occurs. The heats of adsorption of argon at 78°C on Spheron-6 blacks heated up to 2,700°C have been measured calorimetrically.\[^{[37]}\] As shown in Figure 53, the heat of adsorption at low coverages on the raw black is seen to rise sharply to about 3.8 kcal/mole. On the black heated to 2,700°C (called Graphon by surface chemists), the heat of adsorption at very low cover-
ages is only about 2.7 kcal/mole. The increase in heat of adsorption due to adsorbate interaction becomes progressively more prominent as the black is heated to higher temperatures, because the effect is less obscured by a decreasing heat of adsorption due to surface heterogeneity.

![Graph showing changes in surface homogeneity of Graphon upon oxidation as followed by heats of adsorption](image)

**Fig. 53.** Change in surface homogeneity of Graphon upon oxidation as followed by heats of adsorption.\(^{[57]}\)

In the third method it is reasoned that, on a completely homogeneous surface, the adsorption isotherm at very low coverages should be linear and go through the origin.\(^{[58]}\) On the other hand, for a heterogeneous surface the adsorption volume should increase more rapidly with increasing adsorption pressure at very low coverages, until the strong
sites are covered; the isotherm should then become linear. The volume of strong sites is given by the intercept that is obtained upon extrapolating the linear portion of the isotherm back to zero pressure. This technique has been used on original and oxidized Graphon by following the adsorption of nitrogen at 78°K. Figure 54 shows the low-pres-

![Graph](image-url)

**Fig. 54.** Change in surface homogeneity of carbon black upon heat treatment as followed by adsorption at very low coverages.

sure end of the isotherm for the original Graphon and the sample oxidized to 8.5% weight loss. The original Graphon has a negligible amount of strong sites as measured by this method. On the other hand, after 8.5% burn-off, the strong site area has increased to 1.6% of the total surface area. Oxidation is probably increasing the strong site area through exposure of the edges of layer planes, by reacting away carbon atoms at the intersections of the polygonal surfaces and/or within the layer planes (pitting).

Smith and Polley have investigated the effect of heat
treatment of a large thermal black (similar to that shown in Fig. 49) on the increase in its surface area upon oxidation. Figure 55 summarizes the results. The original black

![Graph showing effect of heat treatment on surface area of carbon black]

Fig. 55. Effect of heat treatment on the efficiency of activation of carbon black.

undergoes a large increase in area, whereas the black heated to 2,700° increases in area to about the extent that the geometric area increases by virtue of a decrease in particle size. This study was selected because it illustrates one of the main principles in the production of an activated carbon of high surface area. The raw material to be converted to activated carbon should have small, poorly oriented crystallites.

Electrical and thermal properties of carbon blacks. Because carbon black particles are essentially spherical in shape, the electrical resistivity and thermal conductivity are highly isotropic for bodies made from loose black or from carbon blacks plus a binder. Blacks range widely in their electrical and thermal properties with variations in particle size, amount of volatile matter, and extent of porosity. It is
not the intent here to review all such data. Rather, several points of particular interest will be considered.

Chamberlin,\cite{52} among others, has measured the electrical resistivity of compacted carbon blacks after their heat treatment to different temperatures. Figure 56 presents results on the same channel black discussed in Figure 51,

Fig. 56. Effect of heat treatment on the electrical resistivity of carbon black.\cite{52}

where the black is held under a pressure of 2,500 psi. Even though there is a progressive increase in crystallite size with increase in heat-treatment temperature, the electrical resistivity goes through a pronounced minimum at about 1,300°C. This general shape of curve is characteristic of that found for many carbon blacks. It is reasoned that the minimum is caused by the production of a large concentration of positive holes\cite{41} in the black upon the removal of
volatile matter. Upon heat treatment to higher temperatures, the positive hole concentration is decreased, as crystallites continue to grow.

Carbon blacks are widely used as insulation. It is of interest that a high-porosity channel black, packed to an apparent density of 0.2 g/cc, has a room-temperature thermal conductivity of only $2 \times 10^{-4}$ watt/cm/°C.[62]

*Pyrolytic Carbon*

*History and method of preparation.* Recent accomplishments in the production of massive pyrolytic carbon (PC) shapes constitute an important chapter in materials science and technology. PC can be defined as that material produced from the decomposition of a carbonaceous gas and deposited on a substrate. Most commonly, the gas is methane or natural gas, but acetylene, carbon suboxide, and other gases have been used. PC is an old material. Sawyer[63] described its formation in a patent in 1880. At about the same time, Edison was depositing PC on lamp filaments. In the early 1940s Christensen[64] described the formation of carbon films which could be used as electrical resistors. Such resistors are in wide use today.

In 1956 the status of PC was this—a material made in relatively thin films on relatively small substrates. Comparatively little research was in progress on its preparation or properties. But the need for a high-temperature material of unusual properties in space-vehicle structures (thermal nose shields, rocket nozzles, leading edges) changed the situation abruptly. Large-scale research and development studies over the last five years have led to the satisfactory production of massive PC bodies of at least $\frac{3}{4}$-inch thickness and many square feet in area. At elevated temperatures these bodies have very desirable properties such as high strength, high emissivity, low permeability to gases, and
large anisotropy in their electrical and thermal properties. Much research is now in progress on upgrading the properties still further by producing alloys of pyrolytic carbon and co-deposited metals.

Mechanism of pyrolytic carbon formation. For formation of satisfactory properties, PC must be deposited from a carbonaceous gas which is at a much reduced pressure. Operation at pressures as low as $10^{-3}$ atm is common. At low pressures the gas phase reactions that produce carbon black are minimized, resulting in an increase in the density and ordering of the crystallites in the carbon deposit.

The intermediate steps involved in the conversion of a carbonaceous gas to PC are not well understood. Usually the substrate (frequently bulk graphite) is heated to a temperature considerably in excess of that of the entering gas. Depending upon the difference in temperature between the substrate and entering gas, the gas pressure, gas flow rate, geometry of the system, and the diffusion coefficients and accommodation coefficients of the gas and its decomposition products, the entering gas will be converted to carbon at some rate and with certain properties. Obviously many dehydrogenation and condensation reactions of the parent hydrocarbon and its decomposition products occur on and close to the surface once the gases have been brought to sufficiently high temperatures after multiple collision with the heated substrate.

The properties of PC films are also determined by the mobility of the carbon fragments on the growing surface at the time of their deposition. The higher their mobility, the larger the crystallite size and the better the crystallite orientation that is attained, because of the ability of the fragments to move to preferred positions of low potential energy rather than remain at the sites at which they are deposited.

Hirt and Palmer[65] have reviewed results for the rate of formation of PC from methane for temperatures up to
1,100°C. They find that the temperature coefficient is large; in terms of an apparent activation energy it yields a value of 104 to 107 kcal. This is close to the dissociation energy of the first C—H bond in methane and suggests that homogeneous unimolecular decomposition of methane in the gas phase determines the deposition rate. In their studies on PC from carbon suboxide (C₄O₂), these workers find an activation energy of 54 kcal, which they feel is a reasonable figure also for the dissociation energy of C₄O₂ into C₂O + CO.

Structure of pyrolytic carbon. The crystallites in good quality PC are well aligned relative to each other and, in turn, are aligned with their layer planes closely parallel to the substrate surface. As a result of good crystallite alignment, PC can be formed with apparent densities as high as 2.22 g/cc, which approaches closely the density of ideal graphite. The density of PC varies markedly with deposition temperature at higher gas pressures. For example, Brown and Watt find a steady increase in density from 1.18 to 2.22 g/cc for formation of PC from 0.2 atm of methane between 1,700 and 2,100°C. Diefendorf finds a similar result for deposition from 0.05 atm of methane, but does find that, at a pressure of 2 × 10⁻³ atm, the density remains at about 2.2 g/cc, independent of substrate temperature. Deposits of low density are attributed to the formation of large carbon black particles in the gas phase and their inclusion within the film.

Figure 57 is a micrograph of PC deposited on bulk graphite at 1,850°C from 0.5 atm of methane. The difference between the porous, randomly oriented graphite body and the dense, homogeneous PC is evident. A finer grained PC is often desirable. It can be made readily at higher deposition temperatures and lower gas pressures.

The crystallite size of PC depends strongly upon the deposition temperature. With a bulk graphite substrate, the average crystallite sizes of PC produced from methane
Fig. 57. Photomicrograph of pyrolytic carbon deposited on bulk graphite: $\times 250$.\(^{1081}\)
are below 100 Å for deposition at 1,700°C and increase to about 150 to 300 Å for deposition between 1,900 and 2,500°C. Heat treatment of PC between 2,500 and 3,000°C further improves crystallite alignment and increases crystallite size. That PC is highly graphitizable is to be expected because of its good crystallite alignment. For example, heat treatment of PC (formed at 1,000°C from anthracene) to 2,650°C produced a carbon having an interlayer spacing of 3.3567 Å, or a fraction of displaced layers of only 0.1. It is found that, in PC heated to 3,250°C, crystallites are aligned to better than 1°. Such material can be classified as mosaic single crystals. The availability of such material in convenient shapes should be of considerable importance in studying the solid-state properties of graphite.

The substrate on which PC is deposited can also have an effect on its crystallite size. PC films were formed from carbon suboxide at 700°C over porcelain, copper, platinum, and nickel substrates. Figure 58 A is a transmission electron diffraction pattern of the film deposited over the first three substrates. Diffuse halos, corresponding to a small crystallite-size, turbostratic carbon, are found. On the other hand, the diffraction pattern of the carbon deposited on the nickel substrate (Fig. 58 B) is characteristic of a material of substantial crystallite size having extensive layer plane ordering. Similar diffraction patterns for the carbon films deposited on the former substrates are obtained only upon their heat treatment to temperatures in excess of 2,000°C.

Electrical and thermal properties of pyrolytic carbons. Because of the high degree of crystallite alignment in PC, its electrical and thermal properties are highly anisotropic. Consider good PC deposited around 2,500°C: typical room-temperature electrical resistivities are $3 \times 10^{-4}$ and 0.5 ohm cm, respectively, in directions parallel to and perpendicular to the substrate surface. Thus the ratio of electrical
Fig. 58. Transmission electron diffraction patterns showing effect of substrates on development of crystallinity in pyrolytic carbon: (A) porcelain, copper, or platinum; (B) nickel.\textsuperscript{171}
resistivities is at least 1,000. Typical room temperature thermal conductivities are 3 and 0.03 watts/cm/°C respectively, parallel to and perpendicular to the substrate surface. The ratio of thermal conductivities is about 100, which is considerably higher than that reported for single crystals. It is suggested \(^{[20]}\) that, in single crystals, the thermal conductivity perpendicular to the layers is relatively high because of spiral dislocations which provide paths between the layers.

With the very high anisotropy in thermal conductivity of PC and some of its other properties, it makes an almost ideal nose-cone material for space vehicles. On account of air friction, a nose cone is subjected to large amounts of heat concentrated in a small area. Carbon has a high emissivity and thus efficiently loses by radiation some of the heat produced. The remainder of the heat is primarily lost by conduction away from the cone (parallel to the surface) to a large area of the space vehicle where it, too, is radiated away. Little heat travels through the nose cone to damage sensitive instruments and lower melting-point materials.

Because of its negligible porosity, PC has a very low permeability to gases. This has prompted the coating of uranium carbide fuel particles (used in nuclear reactors) with PC. The carbon serves both as a moderator of fast neutrons and as a coating that captures dangerous fission by-products, thereby preventing them from getting into the main coolant stream.

**Other Carbons**

There are many other ways to prepare carbons with interesting and different properties in addition to those already described. Some of these approaches will be discussed briefly.

*Evaporated carbon films.* Bradley \(^{[72]}\) developed a tech-
nique for producing thin carbon films by the rapid evapora-
tion of bulk carbon. These films are very satisfactory as
replicas of surfaces in electron microscopy studies. Carbon
is evaporated by passing a large current through two
pointed carbon rods, with the points held lightly together.
Intense local heating at the points results in evaporation of
the carbon, some of which travels to and deposits on a sub-
strate some distance away. These films consist of small crys-
tallites.

Surprisingly little has been reported to date on studies
concerned with modifying the properties of evaporated
carbon films, even though many appealing possibilities
exist for doing so. The crystallite size, crystallite orienta-
tion, and film purity can be varied by changing the rate of
evaporation, distance between the source and substrate,
substrate temperature and material, and type and pressure
of atmosphere in the evaporator. Films can be doped with
metallic impurities by their concurrent evaporation. The
structure of films can also be changed by heating them to
elevated temperatures after evaporation.¹³¹

Deitz and McFarlane¹³¹ showed the interesting possi-
bilities of modifying the structure of evaporated carbon
films by varying the pressure in the evaporator. They evap-
orated carbon onto a substrate held at 78⁰K. In runs 1 and
2, the films were prepared under vacuum and under an
initial pressure of 100 microns of krypton respectively.
The film formed in run 1 had a characteristic metallic
luster; that formed in run 2 had a dull luster and an opaque
black appearance. Adsorption isotherms were run on the
films at 78⁰K. The films prepared under vacuum had a sur-
face area of about 1 m²/g, compared to an area of about
1,000 m²/g for the film prepared under a krypton pressure.

Artificial graphite single crystals. Acheson¹³¹ found that
at temperatures above 2,000⁰C silicon carbide decomposes,
leaving highly graphitic carbon. He concluded that carbide
formation is a necessary intermediate step in the graphitization of carbon. Even though this is now known not to be the case, it is true that carbon of higher layer ordering can be formed through the decomposition of certain carbides than can be formed at equivalent temperatures by graphitization of pure carbon materials. For example, aluminum carbide can be decomposed readily to form large single crystals of graphite at 2,500°.17 These crystals have an interlayer spacing of 3.3542 ± 0.0005 Å at 15°C, or complete three-dimensional ordering.

Large graphite crystals can also be grown from an iron melt saturated with carbon. Cooling the surface of such a melt causes precipitation of single crystals that float to the surface. Purification of these crystals with HCl and HF at room temperature or heat treatment to 2,800°C yields a carbon with an interlayer spacing of 3.3540 Å at 15°C.16 In recent studies, single-crystal graphite films were produced in graphite crucibles on the surfaces of melts of tungsten, zirconium carbide, nickel, chromium, rhenium, and molybdenum.175

Colloidal carbons. Carbons that resemble carbon black can be formed in flames in which the hydrocarbon is reacted with chlorine instead of oxygen.174 In the case of methane, carbon is produced by the over-all reaction, \( \text{CH}_4 + 2\text{Cl}_2 \rightarrow \text{C} + 4\text{HCl} \). The carbons produced contain varying amounts of chlorine depending upon the incoming chlorine-hydrocarbon ratio. For example, for ratios of 1.3 and 2.0, carbons containing 9.4 and 45.1% chlorine, respectively, can be formed. The “chlorocarbons” are black in color, have no appreciable odor, and resist oxidation better than the usual carbon blacks.

Colloidal carbon can also be prepared by using a plasma flame. That is, gas can be heated to very high temperatures when passed through an electric arc. A hydrocarbon can then be added to the hot primary gas stream, to be heated
and decomposed to carbon. This is an interesting process, since such carbons can be formed at temperatures above 2,000°C in the absence of oxygen.

Carbon of highly interesting properties (called CMC) can be formed by the decomposition of carbon monoxide-

Fig. 59. Dark-field electron micrograph of carbon produced by decomposition of carbon monoxide over iron; × 25,000. [77]
hydrogen mixtures at atmospheric pressure over finely divided iron.\textsuperscript{[77, 78]} The temperature at which the maximum deposition rate occurs depends upon the CO—H\textsubscript{2} ratio, but a temperature between 500 and 600°C is commonly used. Figure 59 is a dark-field electron micrograph of the raw carbon (78\% C—22\% Fe) formed at 528°C from a 98.6\% CO—1.4\% H\textsubscript{2} mixture. The carbon frequently grows as two filaments, sometimes tightly twisted into a rope and other times not twisted. At the end of the carbon growths there is invariably located a particle of iron, which presumably is the catalyst for the formation of the particular filament. The carbon has an unusually large crystallite size, considering its formation temperature, but the packing of the crystallites is very random and loose. Table 13 presents some data on the crystallite size and surface area (from gas adsorption of nitrogen at 78°C) for a number of carbons that we have discussed. From the crystallite size and true density of each carbon, a crystallite surface area can be calculated. The extreme range in the ratio of crystallite area to gas adsorption area is seen. Most of the crystallite area is available to the adsorbate in the case of CMC. On the other hand, a negligible amount of crystallite area is available in the case of good pyrolytic carbon.

Because of its low crystallite alignment, it would be expected that CMC would graphitize poorly. This is the case. Heat treatment of the sample in Table 13 to 3,000°C increased its crystallite height only to 270 Å and decreased its interlayer spacing from 3.373 to 3.371 Å. That is, the sample still had about 40\% stacking disorder.

\textit{Molecular sieve carbons.} Polymers can be pyrolyzed and converted into carbons of varying yields and structures. An interesting case in point is polyvinylidene chloride (CH\textsubscript{2}—CCL\textsubscript{2})\textsubscript{n}. Upon slow heat treatment to 600°C, the polymer loses hydrogen chloride and is converted into a carbon having a surface area of 1,300 m\textsuperscript{2}/g.\textsuperscript{[79]} The majority of its
pores have diameters in the range of 7 to 8 Å. Adsorption of hydrocarbons on the carbon is activated, with the speed of adsorption depending upon the size of the hydrocarbon.\(^{180}\) It has been concluded\(^{181}\) that this material has only about 25\% of its carbon in the form of parallel-layer planes. The remainder consists of single-layer planes and disorganized carbon.

**Table 13. Comparison of Crystallite Surface Area with Gas Adsorption Surface Area for Different Carbons**

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Crystallite Size, Å</th>
<th>Temperature, °C</th>
<th>Height</th>
<th>Diameter</th>
<th>Area, m²/g</th>
<th>Crystallite Gas ads.</th>
<th>Gas ads. area</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC</td>
<td></td>
<td>528</td>
<td>87</td>
<td>174</td>
<td>200</td>
<td>144</td>
<td>1.4</td>
</tr>
<tr>
<td>Fine channel black</td>
<td></td>
<td>1,000</td>
<td>7</td>
<td>12</td>
<td>2,800</td>
<td>1,000</td>
<td>2.8</td>
</tr>
<tr>
<td>Furnace thermal black</td>
<td></td>
<td>1,200</td>
<td>17</td>
<td>28</td>
<td>1,300</td>
<td>15</td>
<td>87</td>
</tr>
<tr>
<td>Petroleum coke</td>
<td></td>
<td>600</td>
<td>25</td>
<td>35</td>
<td>900</td>
<td>0.5</td>
<td>1,800</td>
</tr>
<tr>
<td>Film carbon</td>
<td></td>
<td>1,000</td>
<td>21</td>
<td>30</td>
<td>1,000</td>
<td>&lt;0.1</td>
<td>&gt;10,000</td>
</tr>
</tbody>
</table>

**REFERENCES**

47. George Porter, "AGARD Memorandum, AG 15/B/49 (1954).
78. Ibid., 140 (1959).