CARBON

1. Introduction

Elemental carbon [7440-44-0], atomic number six in the periodic table, at wt 12.011, occurs naturally throughout the world in either its crystalline, more ordered, or amorphous, less ordered, form. Carbonaceous materials such as soot or charcoal are examples of the amorphous form whereas graphite and diamond are crystalline. Activated carbon is a predominately amorphous solid that has an extraordinary surface area and same volume. See the article CARBON ACTIVATED for a detailed discussion. Carbon atoms bond with other carbon atoms as well as with other elements, principally hydrogen, nitrogen, oxygen, and sulfur, to form carbon compounds, which are the subject of organic chemistry. In its many varying manufactured forms, carbon and graphite can exhibit a wide range of electrical, thermal, and chemical properties that are controlled by the selection of raw materials and thermal processing during manufacture (1) (See GRAPHITE, ARTIFICIAL; GRAPHITE, NATURAL.)

There are two allotropes of carbon: diamond and graphite. The diamond, or isotropic form, has a crystal structure that is face-centered cubic with interatomic distances of 0.154 nm. Each atom is covalently bonded to four other carbon atoms in the form of a tetrahedron. The nature of the bonding explains the differences in properties of the two allotropic forms. The hardness of diamond is derived from the regular three-dimensional network of σ-bonds (see DIAMOND, NATURAL and DIAMOND, SYNTHETIC). Graphite, or the anisotropic form, has a structure that is composed of infinite layers of carbon atoms arranged in the form of hexagons lying in planes. The electronic ground state of carbon is $1s^2$, $2s^2$, $2p^2$. In diamond, the $2s$ and $2p$ electrons mix to form four equivalent covalent σ-bonds. In graphite, three of the four electrons form strong covalent π-bonds with the adjacent in-plane carbon atoms. The fourth electron forms a less strong bond between the planes. A wide variety and range of bulk carbon forms are available within the industry. In general, commercial forms are loosely characterized as carbon or graphite, but they are distinctly different. The term *manufactured carbon* refers to a bonded granular carbon body whose matrix has been subjected to a temperature typically between 900 and 2400°C. *Manufactured graphite* refers to a bonded granular carbon body whose matrix has been subjected to a temperature typically in excess of 2400°C. Natural graphite has been known since the Middle Ages, but carbon was first fabricated by H. Davy in his experiments on the electric arc in the early 1800s. The manufacture of artificial graphite came about only at the end of the nineteenth century, preceded by developments in the fabrication of electrodes. The electric resistance furnace enabled the reaching of approximately 3000°C, the temperature necessary for graphitization. A new application for graphite, its use by E. Fermi in the first self-sustaining nuclear reaction, was followed by new fields of research and new markets opened by development of the aerospace industries, including the use of carbon and graphite fibers in composite materials.

2. Crystallographic Structure

There are two allotropes of carbon: diamond [7782-40-3] and graphite [7782-42-5]. The diamond, or isotropic form, has a crystal structure that is face-centered cubic with interatomic distances of 0.154 nm. Each atom is covalently bonded to four other carbon atoms in the form of a tetrahedron. The nature of the bonding explains the differences in properties of the two allotropic forms. The hardness of diamond is derived from the regular three-dimensional network of σ-bonds; the low electrical conductivity results from fixed-bonding electrons between atoms within the diamond lattice (2). Graphite, or the anisotropic form, has a structure that is composed of infinite layers of carbon atoms arranged in the form of hexagons lying in planes. This structure was first proposed in 1924 (3). The stacking arrangement is ABAB with atoms in alternate planes aligning with each other. Interlayer spacing is 0.3354 nm and interatomic distance within the planes 0.1415 nm. The crystal density is 2.25 g/cm^3 compared to 3.51 g/cm^3 for diamond.

A rhombohedral form, which occurs in small proportions with the hexagonal form, has a stacking arrangement of ABCABC. Being less stable, it begins to convert to the hexagonal form above 1300°C (4).

In 1990, a third form of solid carbon was confirmed and designated "buckminsterfullerenes." These 60-carbon (and 78-C) clusters are described as having the shape of a geodesic dome or soccer ball and hence are also known as "bucky balls" (5). See the article, FULLERENES, for a fuel discussion.

The electronic ground state of carbon is $1s^2$, $2s^2$, $2p^2$, ie, there are four electrons in the outer shell available for chemical bonding. In diamond, the $2s$ and $2p$ electrons mix to form four equivalent covalent σ-bonds. In graphite, three of the four electrons form strong covalent π-bonds with the adjacent in-plane carbon atoms. The fourth electron forms a less strong bond of the van der Waals type between the planes. Bond energy between planes is 17 kJ/mol (4 kcal/mol) (6) and within planes 477 kJ/mol (114 kcal/mol) (7). The weak forces between planes account for such properties of graphite as good lubricity and the ability to form interstitial compounds, whereas the strong π-bonding within the planes contributes to the high electrical and thermal conductivity.

3. Terminology

A wide variety and range of bulk carbon forms are available within the industry. In general, commercial forms are loosely characterized as carbon or graphite, but they are distinctly different. In the United States, the ASTM has issued definitions of terms that relate to manufactured carbon and graphite including processing and property definitions (8). The term manufactured carbon (sometimes called formed carbon, amorphous carbon, or baked carbon) refers to a bonded granular carbon body whose matrix has been subjected to a temperature typically between 900 and 2400°C (8). The process involves mixing carbonaceous filler materials, such as petroleum coke, carbon blacks, or anthracite coal, with binder materials of coal tar or petroleum pitch, forming these mixtures by molding or extrusion, and baking the mixtures in furnaces at temperatures from 900 to 2400°C. Green carbon refers to formed carbonaceous material that has not been baked.

Manufactured graphite (sometimes called synthetic, artificial graphite, electrographite, or graphitized carbon) refers to a bonded granular carbon body whose matrix has been subjected to a temperature typically in excess of 2400°C and whose matrix is thermally stable below that temperature (8). This higher temperature processing, known as graphitization changes not only the crystallographic structure but the physical and chemical properties as well.

Pyrolytic carbons are carbon materials deposited on a heated graphite substrate, or other material, by chemical vapor deposition (CVD) at 800–2300°C; pyrolytic graphite is the product that results from higher temperature treatment and has a crystallite interlayer spacing similar to that of ideal graphite (9). Carbon or graphite fiber forms are produced principally from polyacrylonitrile (PAN) or pitch and are designated carbon or graphite based on crystallographic structure.

Whereas the foregoing are the forms most commonly found in many applications in industry, there are definitions that are necessary not only for industrial purposes but also for consistency in the study of carbon science. Since 1975, the International Committee for Characterization and Terminology of

Carbon has been working to establish definitions and in 1982 published its 30 tentative definitions followed by periodic issues of further tentative definitions (10).

4. History of the Industry

Natural graphite has been known since the Middle Ages for its use in making clay–graphite crucibles and for its lubricating properties. The first known use was for drawing or writing, and it was because of this attribute that the German mineralogist, A. G. Gerner, named graphite after the greek word "graphein" which means to write (11).

Manufacture of artificial graphite did not come about until the end of the nineteenth century. Its manufacture was preceded by developments mainly in the fabrication and processing of carbon electrodes. H. Davy is credited with using the first fabricated carbon in his experiments on the electric arc in the early 1800s. During the nineteenth century, several researchers received patents on various improvements in carbon electrodes. The invention of the dynamo and its application to electric current production in 1875 in Cleveland, Ohio, by C. F. Brush, provided a market for carbon products in the form of arc-carbons for street lighting. The work of a Frenchman, F. Carre, in the late nineteenth century, established the industrial processes of mixing, forming, and baking necessary for the production of carbon and graphite (12).

A significant development occurred when E. G. Acheson patented an electric resistance furnace capable of reaching approximately 3000°C, the temperature necessary for graphitization (13). This development was the beginning of a new industry in which improved carbon and graphite products were used in the production of alkalies, chlorine, aluminum, calcium and silicon carbide, and for electric furnace production of steel and ferroalloys. In 1942, a new application for graphite was found when it was used as a moderator by E. Fermi in the first self-sustaining nuclear chain reaction (14). This nuclear application and subsequent use in the developing aerospace industries opened new fields of research and new markets for carbon and graphite. Carbon and graphite fibers and their use in composite materials are examples of a new form and a new industry.

5. Other Forms of Carbon and Graphite

The versatility and uniqueness of carbon and graphite attest to its widespread use for a variety of industrial applications. Several other forms of carbon and graphite (15) are not covered in industrial articles are presented here.

5.1. Flexible Graphite. A useful form of graphite is a flexible sheet or foil. Because of graphite's stability at high temperatures, flexible foil is useful in applications requiring thermal stability in corrosive environments, eg, gaskets and valve packings, and is often used as a replacement for asbestos gaskets. The basic structure of flexible graphite results in both mechanical and sealing characteristics (16) without additives, a decisive advantage over contemporary facing materials which are more dependent on binders and impregnants to generate adequate properties.

A common method of manufacturing flexible graphite (17) involves treating natural graphite flake with an oxidizing agent such as a solution of nitric and sulfuric acid to form an intercalated compound with graphite. Upon heating at high temperature, the intercalants in the graphite crystal form a gas that causes the layers of the graphite to separate and the graphite flakes to expand or exfoliate in an accordionlike fashion in the *c*-direction, ie, the direction perpendicular to the crystalline planes of the graphite. The expanded flakes are then compressed into sheets which are flexible and can be formed and cut into various shapes. Improvements in the process for reducing material and production costs (18) and a product with enhanced electrical and thermal conductivity properties (19) have been reported.

5.2. Carbon and Graphite Foam.

Carbon–graphite foam is a unique material that has yet to find a place among the various types of commercial specialty graphites. Its low thermal conductivity, mechanical stability over a wide range of temperatures from room temperature to 3000°C, and light weight make it a prime candidate for thermal protection of new, emerging carbon–carbon aerospace reentry vehicles.

The open cell structure of carbon foam with its greater than 90% porosity and chemical inertness at temperatures below 500°C suggests its use as a filtration media for corrosive liquids and a dispersant for gases.

The earliest foamed graphite was made from exfoliated small crystals of graphite bound together and compacted to a low density (20–22). This type of foam is structurally weak and will not support loads of even a few newtons per square meter. Carbon and graphite foams have been produced from resinous foams of phenolic or urethane base by careful pyrolysis to preserve the foamed cell structure in the carbonized state. These foams have good structural integrity, eg, a typical foam of 0.25 g/cm^3 apparent density has a compressive strength of 9.3–15 MPa (1350–2180 psi) with thermal conductivity of 0.87 W/(m·K) at 1400°C. These properties make the foam attractive as a high temperature insulating packaging material in the aerospace field and as insulation for high temperature furnaces. Variations of the resinous-based foams include the syntactic foams where cellular polymers or hollow carbon spheres comprise the primary volume of the material bonded and carbonized in a resin matrix. Use and production of a carbon-graphite foam as a temperature regulator in engines has been reported (23).

5.3. Pyrolytic Graphite.

Pyrolytic graphite was first produced in the late 1800s for lamp filaments. Today, it is produced in massive shapes, used for missile components, rocket nozzles, and aircraft brakes for advanced high performance aircraft. Pyrolytic graphite coated on surfaces or infiltrated into porous materials is also used in other applications, such as nuclear fuel particles, prosthetic devices, and high temperature thermal insulators.

Of the many forms of carbon and graphite produced commercially, only pyrolytic graphite (24,25) is produced from the gas phase via the pyrolysis of hydrocarbons. The process for making pyrolytic graphite is referred to as the chemical vapor deposition (CVD) process. Deposition occurs on some suitable substrate, usually graphite, that is heated at high temperatures, usually in excess of 1000°C, in the presence of a hydrocarbon, eg, methane, propane, acetylene, or benzene.

The largest quantity of commercial pyrolytic graphite is produced in large, inductively heated furnaces in which natural gas at low pressure is used as the source of carbon. Deposition temperatures usually range from 1800 to 2000°C on a deposition substrate of fine-grain graphite.

The properties of pyrolytic graphite exhibit a high degree of anisotropy. For example, the tensile strength in the *ab* direction is five to ten times greater than that of conventional graphite and the strength in the *c* direction is proportionately lower. Similarly, the thermal conductivity of pyrolytic graphite in the *ab* direction ranks among the highest of elementary materials, whereas in the *c* direction its thermal conductivity is quite low. At room temperature, the thermal conductivity values in the *ab* direction are three hundred times greater than in the *c* direction. Pyrolytic graphite with a density of 2.0–2.1 g/cm^3 is the most dense of the commercially produced graphites, exhibiting low porosity and low permeability.

A special form of pyrolytic graphite is produced by annealing under pressure at temperatures above 3000°C. This pressure-annealed pyrolytic graphite exhibits the theoretical density of single-crystal graphite, and though the material is polycrystalline, the properties of the material are close to single-crystal properties. The highly reflective, flat faces of pressure-annealed pyrolytic graphite have made the material valuable as an x-ray monochromator (see X-RAY TECHNIQUES).

5.4. Glassy Carbon. Glassy, or vitreous, carbon is a black, shiny, dense, brittle material with a vitreous or glasslike appearance (26,27). It is produced by the controlled pyrolysis of thermosetting resins; phenol–formaldehyde and polyurethanes are among the most common precursors. Unlike conventional artificial graphites, glassy carbon has no filler material. The liquid resin itself becomes the binder.

There is little crystal growth during carbonization, which always occurs in the solid phase. The solid cross-linking that occurs at this time does not lend itself to crystal growth. The glassy carbons are composed of random crystallites of the order of 5.0 nm across and are not significantly altered by ordinary graphitization heat treatment to 2800°C.

The properties of glassy carbon are unlike those of conventional carbon and graphites. Exhibiting a density of 1.4–1.5 gm/cm^3, they have low open porosity and low permeability. The hardness and brittleness of this material is the same as that of ordinary glass. Chemical inertness and low permeability have made glassy carbon a useful material for chemical laboratory crucibles and other vessels. It is used as a container/heater for the epitaxial growth of silicon crystals and as crucibles for the growth of single crystals. This type of carbon is useful for metallurgical crucibles (26), heating elements, heat-resistant tubes, machine parts, and electrical parts. A composite glassy carbon disk substrate for a data storage device has been reported (29).

5.5. Carbon and Graphite Paper. Carbon and graphite paper is produced from carbon fibers by conventional papermaking methods. The carbon or graphite fibers are cut or chopped to a size suitable for processing, about one-fourth inch in length, homogeneously intermixed with water and a starch binder to form an aqueous slurry, and then deposited from the slurry on a substrate to form a sheet. The sheet is then processed by conventional papermaking techniques to produce a carbon or graphite paper.

This form of carbon and graphite has outstanding electrical conductivity, corrosion resistance, and moderately high strength. These properties have promoted its use in electrodes for electrostatic precipitators. Composites made of laminated carbon paper (30) are excellent high temperature thermal insulators, having a thermal conductivity of less than 1.4 W/(m · K) (0.8 (BTU · ft)/(ft^2 · h · °F)) at room temperature. The material is not substantially affected by being subjected to high temperature. The thermal conductivity increases to 0.5 W/(m · K) (0.3 (BTU · ft)/(ft^2 · h · °F)) at 2000°C, but is still significantly low, particularly in view of its low density (0.5 g/mL).

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