Kirk-Othmer Encyclopedia of Chemical Technology.

GRAPHITE, SPECIALTY

The versatility and uniqueness of carbon and graphite attest to its widespread use for a variety of industrial applications. Several other forms of graphite (1), which have not been fully exploited, are characteristically high in cost but their properties are intriguing enough that applications are continually being found, resulting in further development of new emerging industries.

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 (2) 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 (3) 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 (4) have been reported.

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 (5–7). This type of foam is structurally weak and will not support loads of even a few newtons per square meter. More recently, 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 (see Insulation, thermal). 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.

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 (8, 9) 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 technology).

4. Glassy Carbon

Glassy, or vitreous, carbon is a black, shiny, dense, brittle material with a vitreous or glasslike appearance (10, 11). 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. Also, this type of carbon is useful for metallurgical crucibles (12), heating elements, heat-resistant tubes, machine parts, and electrical parts.

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 (13) are excellent high temperature thermal insulators, having a thermal conductivity of less than 1.4 W/$(\mathrm{m{\cdot}K})$ (0.8 $(\mathrm{BTU{\cdot}ft})/(\mathrm{ft^2{\cdot}h{\cdot}{^\circ}F})$ at room temperature. The material is not substantially affected by being subjected to high temperature. The thermal conductivity increases to 0.5 W/$(\mathrm{m{\cdot}K})$ (0.3 $(\mathrm{BTU{\cdot}ft})/(\mathrm{ft^2{\cdot}h{\cdot}{^\circ}F})$ at 2000°C, but is still significantly low, particularly in view of its low density (0.5 g/mL).

BIBLIOGRAPHY

"Baked and Graphitized Products, Uses" under "Carbon" in *ECT* 2nd ed., Vol. 4, pp. 202–243, by W. M. Gaylord, Union Carbide Corp.; "Other Forms of Carbon and Graphite: Carbon" under "Carbon (Carbon and Artificial Graphite)" in *ECT* 3rd ed., Vol. 4, pp. 628–631, by R. M. Bushong, Union Carbide Corp.

Cited Publications

1. R. W. Cahn and B. Harris, *Nature (London)* **221**, 132 (Jan. 11, 1969).
2. R. A. Mercuri, R. A. Howard, and J. J. McGlamery, *Advanced High Temperature Test Methods for Gasket Materials, Automotive Eng.* **97**, 49–52 (July 1989).
3. U.S. Pat. 3,404,061 (Oct. 10, 1968), J. H. Shane, R. J. Russell, and R. A. Bochman (to Union Carbide Corp.).
4. U.S. Pat. 4,895,713 (Jan. 23, 1990), R. A. Greinke, R. A. Mercuri, and E. J. Beck (to Union Carbide Corp.).
5. R. A. Mercuri, T. R. Wessendorf, and J. M. Criscione, *Am. Chem. Soc. Div. Fuel Chem. Prepr.* **12**(4), 103 (1968).
6. C. R. Thomas, *Mater. Sci. Eng.* **12**, 219 (1973).
7. S. T. Benton and C. R. Schmitt, *Carbon* **10**, 185 (1972).
8. J. C. Bokros, *Chem. Phys. Carbon* **5**, 1 (1969).
9. A. W. Moore, *Chem. Phys. Carbon* **11**, 69 (1973).
10. F. C. Cowtard and J. C. Lewis, *J. Mater. Sci.* **2**, 507 (1967).
11. G. M. Jenkins and K. Kawamura, *Polymeric Carbons–Carbon Fiber, Glass, and Char.*, Cambridge University Press, New York, 1976, 178 pp.

12. C. Nakayama and co-workers, *Proceedings of the Carbon Society of Japan*, Annual Meeting, 1975, p. 114; C. Nakayama, M. Okawa, and H. Nageshima, *13th Biennial Conference on Carbon, 1977*, Extended Abstracts and Program, American Carbon Society, Irvine, Calif., 1977, p. 424.
13. U.S. Pat. 3,844,877 (Oct. 29, 1974), T. R. Wessendorf and J. M. Criscione (to Union Carbide Corp.).

J. M. CRISCIONE
UCAR Carbon Company Inc.

Related Articles

Graphite, artificial; Insulation, thermal; Carbon, Structure, Terminology, and History; Graphite, Artificial; Graphite, Processing Artificial; Graphite, Properties of Artificial; Graphite, Applications of Artificial