

GRAPHITE, ARTIFICIAL

1. Introduction

The manufactured form of carbon and graphite is discussed within this article. 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.

Table 1. Properties of Graphite Crystals at Room Temperature^a

Property	Value in basal plane	Value across basal plane
resistivity, $\mu\Omega \cdot \text{m}$	0.40	ca 60
elastic modulus, GPa ^b	1020	36.5
tensile strength (est), GPa ^b	96	34
thermal conductivity, W/(m · K)	ca 2000	10
thermal expansion, °C ⁻¹	-0.5×10^{-6}	27×10^{-6}

^aRef. 1.^bTo convert GPa to psi, multiply by 145,000.

2. Physical Properties

The graphite crystal, the fundamental building block for manufactured graphite, is one of the most anisotropic bodies known. Properties of graphite crystals illustrating this anisotropy are shown in Table 1 (1). Anisotropy is the direct result of the layered structure with extremely strong carbon-carbon bonds in the basal plane and weak bonds between planes. The anisotropy of the single crystal is carried over in the properties of commercial graphite, though not nearly to the same degree. By the selection of raw materials and processing conditions, graphites can be manufactured with a very wide range of properties and degree of anisotropy. The range of room temperature properties, attainable for various forms of graphite, is shown in Figures 1 and 2 (1). The range extremities represent special graphites having limited industrial utility, whereas the bulk of all manufactured graphites fall in the bracketed areas marked conventional.

The directional properties of manufactured graphite arise in the following way. When the coke aggregate is crushed and sized, the resulting coke particles tend to have one axis longer than the other two. As the plastic mix of particles and binder pitch is formed into the desired shape, the long axis of particles tends to align perpendicularly to the molding force in molded graphite and parallel to the extrusion force in extruded graphites. The particle alignment is preserved during the subsequent processing so that properties of the finished graphite have an axis of symmetry that is parallel to the forming force. Properties in the plane perpendicular to the axis of symmetry are essentially independent of direction. Samples cut parallel to the molding force for molded graphites or perpendicular to the extrusion force for extruded graphites are designated as cross-grain. Samples cut parallel to the molding plane of molded graphites or parallel to the extrusion axis for extruded graphites are designated as with-grain. A number of special test procedures for determining the properties of carbon and graphite have been adopted by ASTM (2).

Manufactured graphite is a composite of coke aggregate (filler particles), binder carbon, and pores. Most graphites have a porosity of 20–30%, though special graphites can be made that have porosity well outside this range. Manufactured graphite is a highly refractory material that has been thermally stabilized to as high as 3400°C. At temperatures in excess of 3500°C, the vapor pressures of the various carbon species in the manufactured graphite begin to

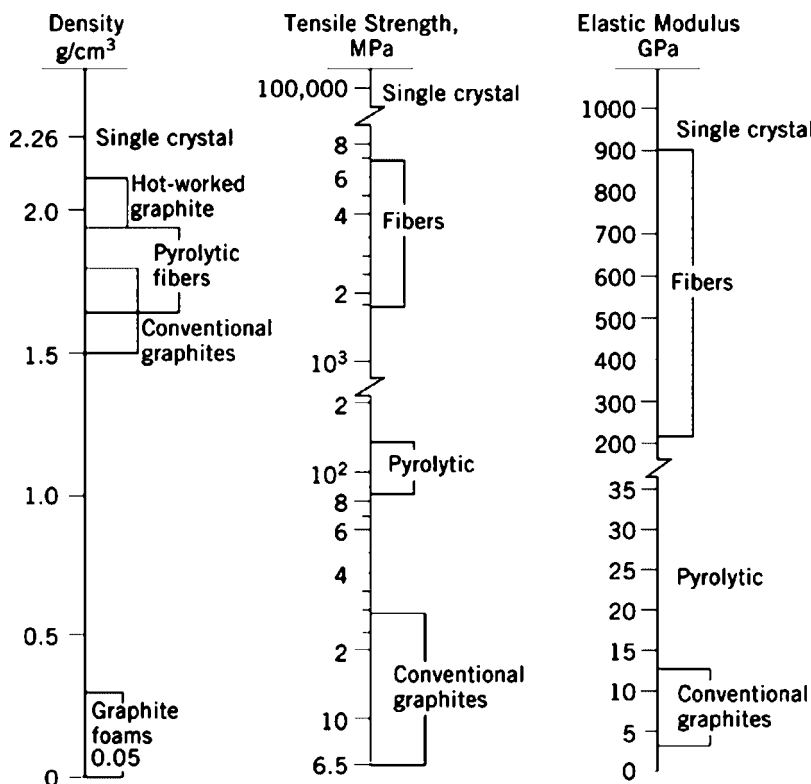


Fig. 1. With-grain mechanical properties of artificial graphite (1). To convert MPa to psi, multiply by 145.

exceed 10 kPa (~ 0.1 atm) and vapor transport occurs. The strength of graphite increases with temperature to 2200°C; above 2200°C, graphite becomes plastic and exhibits viscoelastic creep under load (3). Graphite has high resistance to thermal shock, a property that makes it a more valuable structural material at higher temperatures than most metals and alloys. For many applications of graphite, one or more of the following characteristics are important: density, elastic modulus, mechanical strength, electrical and thermal conductivity, and thermal expansion.

2.1. Electrical Properties. Manufactured graphite is semimetallic in character with the valence and conduction bands overlapping slightly (4–6). Conduction is by means of an approximately equal number of electrons and holes that move along the basal planes. The resistivity of single crystals as measured in the basal plane is approximately $0.40 \mu\Omega \cdot \text{m}$; this is several orders of magnitude lower than the resistivity across the layer planes (7–9). Thus the electrical conductivity of formed graphite is dominated by the conductivity in the basal plane of the crystallites and is dependent on size, degree of perfection, orientation of crystallites, and on the effective carbon–carbon linkages between crystallites. Manufactured graphite is strongly diamagnetic and exhibits a Hall effect, a Seebeck coefficient, and magnetoresistance. The green carbon body is

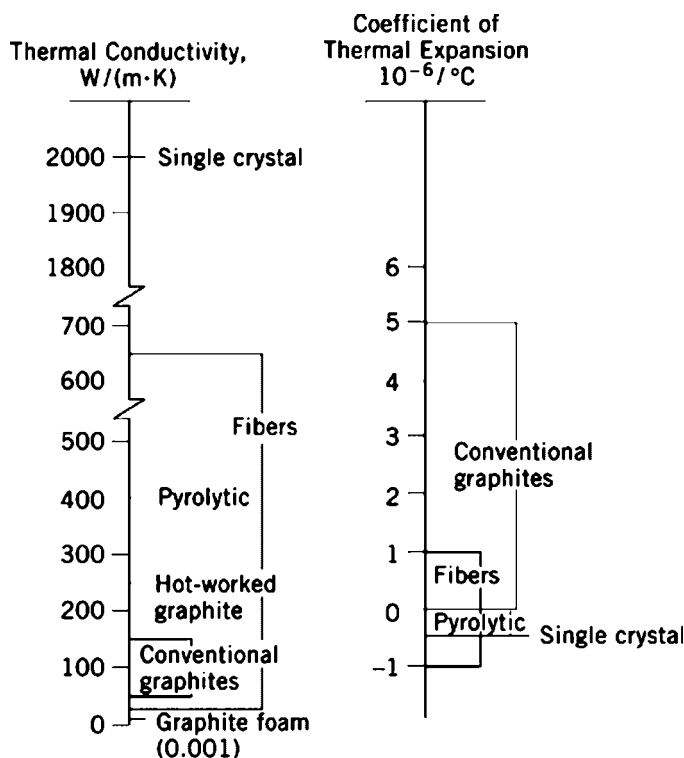


Fig. 2. With-grain thermal properties of artificial graphite (1).

practically nonconductive; however, heat treatment at 800°C decreases the resistivity by several orders of magnitude, and thereafter resistivity decreases slowly. After graphitization to over 2500°C, the room temperature electrical resistivity may range from a few hundred to a few tenths $\mu\Omega \cdot \text{m}$, depending on the type of raw materials used. Graphites made from petroleum coke usually have a room temperature resistivity range of 5 – 15 $\mu\Omega \cdot \text{m}$ and a negative temperature coefficient of resistance to about 500°C, above which it is positive. Graphites made from a carbon black base have a resistivity several times higher than those made from petroleum coke, and the temperature coefficient of resistance for the former remains negative to at least 1600°C.

2.2. Thermal Conductivity. Compared with other refractories, graphite has an unusually high thermal conductivity near room temperature (10); above room temperature, the conductivity decreases exponentially to approximately 1500°C and more slowly to 3000°C (11). With the grain, the thermal conductivity of manufactured graphite is comparable with that of aluminum; against the grain, it is comparable to that of brass. However, graphite is similar to a dielectric solid in that the principal mechanism for heat transfer is lattice vibrations. The electronic component of thermal conductivity is less than 1%. Graphite does not obey the Wiedemann-Franz Law; however, at room temperature the ratio of thermal and electrical conductivities is equal to approximately 0.126 when the

thermal conductivity is in $W/(m \cdot K)$ and the electrical conductivity is in $S(= 1/\Omega)$ (12,13). For most graphites, a value of thermal conductivity at room temperature accurate to $\pm 5\%$ can be obtained from the measured value of the electrical conductivity.

2.3. Coefficient of Thermal Expansion (CTE). The volumetric thermal expansion (VTE) of manufactured graphite expressed in equation 1 is anomalously low when compared to that of the graphite single crystal, where wg designates with-grain and cg, cross-grain.

$$VTE = CTE_{wg} + 2 CTE_{cg} \quad (1)$$

At room temperature, the volume coefficient of thermal expansion of a single crystal is approximately $25 \times 10^{-6}/^{\circ}C$ (14,15), whereas those of many manufactured graphites fall in the range of $4 - 8 \times 10^{-6}/^{\circ}C$. There are exceptions and some commercially available, very fine-grain, near-isotropic graphites have a volumetric expansion as high as two-thirds the value for the single crystal. The low value of volume expansion of most manufactured graphite has been related to the microporosity within the coke particles. The microcracks within the coke particle accommodate the large c -axis expansion of graphite crystallites (16–18) and effectively neutralize it. The coefficient of thermal expansion is somewhat sensitive to the filler particle sizing and to the method of processing, but the anisotropy and perfection degree of filler carbon particles largely determine the expansion characteristics of the finished graphite. Except for differences in absolute values, plots of the CTEs of manufactured graphite versus temperature are essentially parallel to each other, showing that the change in CTE with temperature is approximately the same for all graphites at high temperatures. The mean linear coefficient of thermal expansion between room temperature and any final temperature can be obtained by adding the value of CTE for the temperature interval $20-100^{\circ}C$ to the appropriate factor which varies from 0 at $100^{\circ}C$ to 2.52×10^{-6} at $2500^{\circ}C$ (19). This method is valid for stock of any grain orientation.

2.4. Mechanical Properties. The hexagonal symmetry of a graphite crystal causes the elastic properties to be transversely isotropic in the layer plane; only five independent constants are necessary to define the complete set. The self-consistent set of elastic constants given in Table 2 has been measured in air at room temperature for highly ordered pyrolytic graphite (20). With the exception of c_{44} these values are expected to be representative of those for the

Table 2. Elastic Constants of Graphite^a

$c_{11} = 1.06 \pm 0.002$	$s_{11} = 0.98 \pm 0.03$
$c_{12} = 0.18 \pm 0.02$	$s_{12} = -0.16 \pm 0.06$
$c_{13} = 0.015 \pm 0.005$	$s_{13} = -0.33 \pm 0.08$
$c_{33} = 0.0365 \pm 0.0010$	$s_{33} = 27.5 \pm 1.0$
$c_{44} = 0.00018 - 0.00035$	$s_{66} = 2.3 \pm 0.2$

^aUnits c_{ij} (stiffness constant) in TPa, s_{ij} (compliance constant) in $(GPa)^{-1}$. To convert TPa to psi, multiply by 145,000,000.

graphite single crystal. Low values of shear and cleavage strengths between the layer planes compared with very high C–C bond strength in the layer planes suggest that graphite always fails through a shear or cleavage mechanism. However, the strength of manufactured graphite depends on the effective network of C–C bonds across any stressed plane in the graphite body. Until these very strong bonds are broken, failure by shear or cleavage cannot take place. Porosity affects the strength of graphite by reducing the internal area over which stress is distributed and by creating local regions of high stress. Because of the complexity of the graphite structure, a simple analytical model of failure has not been derived (21). The stress–strain relation for bulk graphite is concave toward the strain axis. The relaxation of the stress leads to a small residual strain; repeated stressing to larger loads followed by gradual relaxation leads to a set of hysteresis loops contained within the stress-strain envelope (3,22–26). Each successive load causes an increase in the residual strain and results in a decreased modulus for the sample. The residual strain can be removed by annealing the sample to the graphitizing temperature after which its original stress–strain response is restored. In the limit of zero stress, the elastic modulus of graphite is the same in compression and tension, and is equal to the modulus derived from dynamic measurements (27). The modulus of graphite is weakly dependent on temperature, increasing with temperature to approximately 2000°C and decreasing thereafter. The strain at rupture of most graphites is 0.1–0.2%; however, values of strain at rupture approaching 1.0% have been obtained for specially processed, fine-grain graphites (28). Graphite exhibits measurable creep under load and at temperatures above 1600°C, but for most applications creep can be neglected below 2200°C. As the temperature is increased above 2500°C, the creep rate increases rapidly and the short-time strength decreases rapidly.

Thermal shock resistance is a primary attribute of graphite and a number of tests have been devised in attempts to establish a quantitative method of measurement (29,30). These tests, which establish very large thermal gradients in small specially shaped samples, continue to give only qualitative data and permit establishment of only the relative order of shock resistance of different graphites. A commonly used thermal shock index is the ratio of the thermal conductivity and strength product to the expansion coefficient and modulus product (31). At high temperatures values of this index for graphite are higher than for any other refractory material. To show the range of property values of graphite, several properties for a very coarse-grain graphite and a very fine-grain graphite are given in Table 3 (27,32).

2.5. Chemical Properties. The impurity (ash) content of all manufactured graphite is low, since most of the impurities originally present in raw materials are volatilized and diffuse from the graphite during graphitization. Ash contents vary from 1.5% for large diameter graphites to less than 10 ppm for purified graphites. Iron, vanadium, calcium, silicon, and sulfur are principal impurities in graphite; traces of other elements are also present (33). Through selection of raw materials and processing conditions, the producer can control the impurity content of graphites to be used in critical applications. Because of its porosity and relatively large internal surface area, graphite contains chemically and physically adsorbed gases. Desorption takes place over a wide tempera-

Table 3. Properties of Fine- and Coarse-Grain Graphites^a

Temp., °C	Thermal conductivity, W/(n · K)		CTE ^b , cm/cm × 10 ⁶ /°C		Specific head ^c , kJ/(kg · K)	Tensile ^d				Compression ^d			
	wg	ag	wg	ag		Modulus, GPa		Strength, MPa		Modulus, GPa		Strength, MPa	
						wg	ag	wg	ag	wg	ag	wg	ag
Fine-grained graphite, 180 μm maximum grain size													
21	150	114	2.15	3.10	0.63	11.5	7.9	17.4	15.0	9.7	7.2	26.6	20.1
260	117	93	2.50	3.46	1.30	11.6	8.0	19.3	17.2	10.0	7.4	27.9	21.7
538	91	72	2.82	3.84	1.63	11.7	8.1	21.7	19.7	10.3	7.6	29.3	23.4
816	73	57	3.16	4.12	1.80	11.9	8.3	24.1	22.1	10.6	7.9	30.9	25.2
1093	60	46	3.45	4.45	1.95	12.1	8.6	26.0	24.3	11.4	8.3	32.4	26.9
1371	52	40	3.70	4.69	2.03	12.5	9.0	28.3	26.2	12.4	9.0	35.2	29.3
1649	46	35	3.95	4.91	2.11	13.2	9.6	29.9	27.9	13.4	9.7	38.1	31.6
1927	42	32	4.17	5.16	2.16	13.7	10.5	31.0	29.3	13.4	9.7	32.2	37.2
2204	40	29	4.35	5.39	2.18	11.5	8.4	31.7	30.1	12.1	9.0	37.9	32.6
2482	38	28	4.58	5.71	2.20	8.0	5.9	31.0	29.3	10.0	7.9	32.4	26.6
2760	36	28	4.83	6.04	2.20	5.2	4.3	26.9	24.8	7.9	6.2	26.6	19.1
Coarse-grained graphite, 6400 μm maximum grain size													
21	156	108	0.46	1.03		4.2	2.6	3.75	2.91	3.0	2.6	9.3	12.1
1371	30	22	2.4	3.2		5.8	2.9	5.34	4.54	3.4	2.8	12.0	14.7
1927	24	19	2.7	2.85		6.5	3.7	5.39	4.36	4.3	3.3	14.1	17.4
2427	24	20	3.0	4.2		5.6	3.0	7.32	5.17				

^awg = with – grain; ag = across – grain.^bCTE = coefficient of thermal expansion.^cTo convert kJ to kcal, divide by 4.184.^dTo convert MPa to psi, multiply by 145.

ture range, but most of the gas can be removed by heating in a vacuum at approximately 2000°C.

Graphite reacts with oxygen to form CO_2 and CO , with metals to form carbides, with oxides to form metals and CO , and with many substances to form laminar compounds (34,35). Of these reactions, oxidation is the most important to the general use of graphite at high temperatures. Oxidation of graphite depends on the nature of the carbon, the degree of graphitization, particle size, porosity, and impurities present (36). These conditions may vary widely among graphite grades. Graphite is less reactive at low temperatures than many metals; however, since the oxide is volatile, no protective oxide film is formed. The rate of oxidation is low enough to permit the effective use of graphite in oxidizing atmospheres at very high temperatures when a modest consumption can be tolerated. A formed graphite body alone will not support combustion. The differences in oxidation behavior of various types of graphite are greatest at the lowest temperatures, tending to disappear as the temperature increases. If an oxidation threshold is defined as the temperature at which graphite oxidizes at 1% per day, the threshold for pure graphite lies in the range of 520–560°C. Small amounts of catalyst, such as sodium, potassium, vanadium, or copper, reduce this threshold temperature for graphite by as much as 100°C but greatly increase the oxidation rate in the range of 400–800°C (33). Above 1200°C, the number of oxygen collisions with the graphite surface controls the oxidation reaction. Oxidation of graphite is also produced by steam and carbon dioxide; general purpose graphite has a temperature oxidation threshold of approximately 700°C in steam and 900°C in carbon dioxide. At very low concentrations of water and CO_2 there is also a catalytic effect of impurities on the oxidation behavior of graphite (37).

3. Raw Materials

The raw materials used in the production of manufactured carbon and graphite largely control the ultimate properties and practical applications of the final product. This dependence is related to the chemical and physical nature of the carbonization and graphitization processes.

Essentially any organic material can be thermally transformed to carbon. The carbonization process through the elimination of heteroatoms and substituent hydrogen converts the organic precursor into a carbon polymer. This polymer consists of aromatic carbons arranged in large polynuclear aromatic ring systems. With continued heat treatment, this carbon is transformed to a more or less ordered three-dimensional framework approaching the structure of graphite. Differences in the final material depend on the ease and extent of completion of these overall chemical and physical ordering processes.

In most carbon and graphite processes, the initial polymerization reactions occur in the liquid state. The subsequent stages of crystal growth, heteroatom elimination, and molecular ordering occur in the solid phase. The result is the development of a three-dimensional graphite structure.

Most of the raw materials in the production of bulk carbon and graphite products are derived from petroleum (qv) and coal (qv). These precursors are generally residual by-products and exhibit a highly aromatic composition. The two

main raw materials for carbon and graphite are pitches and cokes. Pitches are derived from distillation and thermal heat treatment of tars or oils. Pitches are solid at room temperature but soften to a liquid at elevated temperatures. As a result of thermal processing, commercial pitches are extremely complex materials with literally hundreds to thousands of discrete molecular components. These components are predominantly polynuclear aromatic or heterocyclic species with varying degrees of alkyl group substitution. Pitches have a glasslike character, generally exhibit a glass-transition temperature, and soften over a very broad temperature range. The melting temperatures and temperature–viscosity behavior of pitches vary with their processing conditions. Conventional petroleum and coal-derived pitches have average molecular weights of 300–500 and structures containing on the order of 3–12 aromatic rings.

Pitches can be transformed to a mesophase state by further chemical and physical operations. Heat treatment of conventional pitches results in additional aromatic polymerization and the distillation of low molecular weight components. This results in an increase in size and concentration of large planar aromatic molecular species whereupon the precursor pitch is transformed to a mesophase state exhibiting the characteristics of nematic liquid crystals (38). Additional heat treatment converts the mesophase pitch to an infusible aromatic hydrocarbon polymer designated as coke.

Cokes are infusible solids with average molecular weights estimated to be on the order of several thousand. Coke can be described as a thermoset aromatic hydrocarbon polymer. The molecular order and structure of coke is determined by the chemical and physical processes that occur in the liquid mesophase state. Subsequent high temperature heat treatment of coke, as in calcination, induces solid-state polymerization and ordering while removing substituent atoms in the form of gaseous by-products. Sulfur and nitrogen, present in the coke precursor, can be stabilized and incorporated into the aromatic polymer structure at this stage. These heteroatoms evolve rapidly during graphitization by a phenomenon designating as puffing.

Bulk carbon and graphite products, such as electrodes, are produced using calcined coke as a filler and liquid pitch as a binder. After mixing, the blend is molded or extruded to a desired shape and then baked and graphitized to produce the final carbon or graphite product. Although many different raw materials are used in the manufacture of carbon and graphite, the primary materials in terms of total tonnage are calcined petroleum coke used as a filler material and coal-tar pitch as a binder. Petroleum and coal-tar pitches are also utilized as impregnants to strengthen the final graphite artifact. Coal-tar-based coke and anthracite coal are also widely employed as filler materials for carbon and graphite.

High carbon yielding resins are sometimes employed as raw material precursors for specialty carbons. Various chemical additives are also used in low concentrations to improve the processability or to control puffing during graphitization.

3.1. Filler Materials. *Petroleum Coke.* Petroleum coke is the largest single precursor material in terms of quantity for manufactured carbon and graphite products. Commercial coke is produced by the delayed coking of heavy petroleum by-products. Delayed coking technology is currently practiced throughout

the world. Delayed coke can fall into several categories: fuel-grade, aluminum-grade, and coke for carbon and graphite. The coke employed for carbon and graphite includes regular coke and needle coke. Needle or premium coke is used in the production of graphite electrodes for electric arc furnaces whereas regular coke is used for other carbon and graphite products.

The key difference in the production of regular and needle petroleum coke is the feedstock precursor. Needle coke is generally produced from highly aromatic starting materials such as decant oil derived from catalytic cracking of petroleum distillate. Before it is fed to the delayed coker, the decant oil can be pretreated by a hydrodesulfurization (HDS) process to remove sulfur or thermally cracked to a thermal tar to increase carbon yield. Regular and aluminum-grade cokes are generally prepared from the residues (resids) of crude oil distillation. Pyrolysis tars from naphtha or gas-oil cracking can also be employed to produce intermediate-grade cokes, which exhibit more or less needlelike character depending on the tar composition and coke preparation parameters.

Although the feedstock exerts the greatest influence, coke properties are also determined by process variables including coking time and temperature, pressure, and recycle ratio. The most important properties in delayed coke are sulfur level, volatile matter content, ash, coefficient of thermal expansion (CTE), and hardness. The CTE, which is generally measured on an extruded graphite artifact prepared using the coke as a filler, reflects the needlelike character of the coke. Premium cokes for graphite electrodes are anisotropic and have very low CTEs in the extrusion direction. Regular cokes are isotropic and give graphite artifacts with high CTE values.

The sulfur level of cokes is important from an environmental standpoint since sulfur is released during eventual graphitization of the coke-based product. High sulfur cokes also lead to irreversible rapid expansion, puffing, of the synthetic carbon during the graphitization process. Excessive puffing results in lower strength and density and can cause cracks and splits in the graphitized artifact. A high volatile content in the raw coke leads to a degradation in coke density and strength during subsequent calcining. A high ash content is usually undesirable and leads to contamination in the finished product. High ash is particularly detrimental for needle coke feedstock since the ash particles interfere with the coalescence of the mesophase and the development of long-range order and anisotropy. The raw coke must be sufficiently hard to prevent excessive degradation into fines during subsequent calcination.

The selection of petroleum coke for a particular graphite product is based on the combination of these properties. For a premium needle coke, a decant oil feedstock is usually selected or pretreated to give a coke that is low in sulfur, low in ash, and exhibits a low coefficient of thermal expansion. When evaluated as fillers in graphitized artifacts, these cokes give CTE values $< 0.3 \times 10^{-6}/^{\circ}\text{C}$ between 25–100°C. Tars derived from the thermal cracking of gas oils and certain pyrolysis tars can also give needlelike cokes with appropriate processing. A necessary requirement for these feedstocks is that they develop a highly ordered mesophase with large anisotropic domains. During coking, the mesophase is oriented by the gaseous volatiles and shear forces to give the aligned needle coke structure (39).

Cokes derived from resids or blends of resids with other petroleum feedstocks give high CTE values and are utilized as fillers for aluminum anodes and certain specialty carbon and graphite products. The remaining properties differ depending on the final application. A low ash content is required for cokes used in the aluminum industry since these impurities tend to concentrate in the aluminum as the anode is consumed. Impurities that are of particular concern include: vanadium, nickel, iron, and silicon; other impurities such as sulfur are slightly less critical. Since the carbon consumption per kilogram of aluminum produced affects the economics of the process, bulk density and oxidation resistance are also important properties.

Low sulfur and ash levels are required for high CTE, isotropic cokes used for carbon and graphite specialty products. Highly isotropic cokes are also the filler materials for producing graphite for nuclear reactors. The purity, particularly the boron content, is critical in this application. Properties of typical needle and isotropic (regular) cokes are summarized in Table 4

Coal-Tar Pitch Coke. Coal-tar pitch is used to produce needle coke primarily in Japan. Processes for producing needle coke from pitch have also been developed in Germany (41). The key to producing needle coke from coal tar or coal-tar pitch is the removal of the high concentrations of infusible solids, or material insoluble in quinoline (QI), which are present in the original tar. The QI inhibits the growth of mesophase and results in an isotropic, high CTE coke from coal-tar pitch. After removal of the QI, very anisotropic and low CTE cokes are obtained from coal-tar-based materials.

Because of very high aromaticity, high coking value, and excellent coking characteristics, coal tar and coal-tar pitches are very attractive premium coke precursors. The solids removal prior to coking is usually accomplished through filtration with the use of a cosolvent (42). Transformation to coke may employ

Table 4. **Typical Properties of Isotropic and Needle Cokes^a**

Property	Aluminum anode-grade coke		Graphite electrode-grade needle coke	
	Raw	Calcined ^b	Raw	Calcined ^b
sulfur, wt%	2.5	2.5	0.8	0.8
ash, wt%	0.25	0.30	0.10	0.15
vanadium, ppm	150	200	10	10
nickel, ppm	150	200		20–40
silicon, wt%	0.02	0.02	0.04	0.04
volatile matter, wt%	10–12		8	
resistivity, $\mu\Omega\cdot\text{m}$		950		1100
real density, g/cm^3		2.06		2.12
bulk density, g/cm^3		0.80		0.88
coefficient of thermal expansion of graphite per $^{\circ}\text{C}$ (25–100 $^{\circ}\text{C}$)		2×10^{-6}		0.3×10^{-6}

^aRevised data based on Ref. 40.

^bCalcining, discussed later in this section, is a thermal treatment that removes volatiles from the raw materials and shrinks the particles.

different technology from conventional delaying coking. Since coal-tar materials contain substantial quantities of heterocyclic nitrogen, puffing can be a problem during rapid graphitization.

Natural Graphite. Natural graphite is a crystalline mineral form of graphite occurring in many parts of the world (see GRAPHITE, NATURAL). It is occasionally used as a component in carbon and graphite production. Intercalated natural graphite is used to form a flexible graphite product.

Carbon Blacks. Carbon blacks are occasionally used as components in mixes to make various types of carbon products. Carbon blacks are generally prepared by deposition from the vapor phase using petroleum distillate or gaseous hydrocarbon feedstocks (see CARBON BLACK).

Anthracite. Anthracite is preferred to other forms of coal (qv) in the manufacture of carbon products because of its high carbon-to-hydrogen ratio, its low volatile content, and its more ordered structure. It is commonly added to carbon mixes used for fabricating metallurgical carbon products to improve specific properties and reduce cost. Anthracite is used in mix compositions for producing carbon electrodes, structural brick, blocks for cathodes in aluminum manufacture, and in carbon blocks and brick used for blast furnace linings.

Synthetic Resins. Various polymers and resins are utilized to produce some specialty carbon products such as glassy carbon or carbon foam and as treatments for carbon products. Typical resins include phenolics, furan-based polymers, and polyurethanes. These materials give good yields of carbon on pyrolysis and generally carbonize directly from the thermoset polymer state. Because they form little or no mesophase, the ultimate carbon end product is nongraphitizing.

3.2. Binders. Pitches. Carbon articles are made by mixing a controlled size distribution of coke filler particles with a binder such as coal-tar or petroleum pitch. The mix is then formed by molding or extruding and is heated in a packed container to control the shape and set the binder. Thus the second most important raw material for making a carbon article is the pitch binder. The pitch binder preserves the shape of the green carbon and also fluidizes the carbon particles, enabling them to flow into an ordered alignment during the forming process. During the subsequent baking steps, the pitch binder is pyrolyzed to form a coke that bridges the filler particles and serves as the permanent binding material. These carbon bridges provide the strength in the finished article and also provide the paths for energy flow through thermal and electric conductance.

A binder used in the manufacture of electrodes and other carbon and graphite products must: (1) have high carbon yield, usually 40–60 wt % of the pitch; (2) show good wetting and adhesion properties to bind the coke filler together; (3) exhibit acceptable softening behavior at forming and mixing temperature, usually in the range of 90–180°C; (4) be low in cost and widely available; (5) contain only a minor amount of ash and extraneous matter that could reduce strength and other important physical properties; and (6) produce binder coke that can be graphitized to improve the electrical and thermal properties.

The principal binder material, coal-tar pitch, is produced by the distillation of coal tar. Coal tar is obtained primarily as a by-product of the destructive distillation of bituminous coal in coke ovens during the production of metallurgical coke. Petroleum pitch is used to a much lesser extent as a binder in carbon and

graphite manufacture. Because of its low solids content, petroleum pitch is used as an impregnant to strengthen carbon artifacts prior to graphitization.

Pitches are characterized by softening point, carbon yield, solubility in aromatic solvents such as toluene and quinoline, ash, and heteroatom content. Since pitches soften over a broad temperature range, arbitrary methods have been used to define pitch softening point. The Mettler method, ASTM D3104, has been adopted as a standard procedure in the United States. For binder pitches, both the softening point and the viscosity versus temperature behavior are important in determining the forming conditions of the carbon and graphite product. For impregnation, the viscosity temperature dependence controls the impregnation temperature.

Coal-tar binder pitches differ both chemically and constitutionally from petroleum pitches (Table 5). The coal-tar pitches are composed primarily of unsubstituted polynuclear aromatic hydrocarbons and heterocyclics. Substantial quantities of nitrogen-containing compounds, and to a lesser extent sulfur heterocyclics, are present in coal-tar pitch. Coal-tar pitches generally contain substantial quantities of QI. The QI is largely an infusible low temperature carbonaceous solid produced in the coking operation used to generate the precursor tar. Some coal particles and mesophase can also be included in the QI. The QI contributes to the carbon yield of the binder and serves to strengthen the carbon artifact. Excessive amounts of QI adversely affect the rheology of the pitch binder.

Coal-tar binder pitches are produced with varying softening points depending on the application and the carbon-graphite manufacturing process. Typical softening points for binder pitches used in manufacture of graphite electrodes range from about 90–120°C. Higher and lower softening point pitches are used in specialty applications. Coal-tar impregnating pitches with little or no QI are used in Japan and Europe. In Japan, QI removal procedures similar to those

Table 5. Properties of Petroleum Impregnating and Coal-Tar Binder Pitches

Property	Petroleum	Coal tar
Mettler softening point, °C	120	110
sp gr 25°C, g/mL	1.24	1.33
coking value, wt%	51	60
toluene insolubles (TI), wt%	3.6	33
quinoline insolubles (QI), wt%	0.2	14
ash, wt%	0.16	0.10
sulfur, wt%	3.0	0.8
nitrogen, wt%	0.3	1.0
viscosity in Pa·s ^{aaa}		
150°C	15.0	3.6
160°C	4.5	1.5
170°C	1.7	0.8
aromatic H, %	60	90
average molecular weight	500	350

^{aaa}To convert Pa·s to poise, multiply by 10.

used for producing pitch coke are employed. The production and usage of coal-tar pitches as binders for carbon and graphite have been reviewed (43).

In North America, petroleum pitch is used primarily as a carbon impregnating material. The petroleum pitch is prepared by the thermal cracking and distillation of decant oil. The components of petroleum pitch are largely alkyl substituted polynuclear aromatics and heterocyclics. The latter are predominantly sulfur compounds. Unlike coal-tar pitches, petroleum pitches have very low QI contents. The solids in petroleum pitch are mainly catalyst fines that were present in the original decant oil. The principal commercial petroleum impregnant pitch has a Mettler softening point of about 120°C. However, petroleum pitches with softening points as high as 280°C are available for use in certain specialty applications.

Certain compounds found in some coal-tar and petroleum pitches are carcinogenic. Individuals working with pitches or exposed to fumes or dust should wear protective clothing to avoid skin contact. Respirators should be worn when pitch dust or fume concentrations in the air are above established limits.

3.3. Additives. In addition to the primary ingredients, the fillers and binders, minor amounts of other materials are added at various steps in the carbon and graphite manufacturing process. Although the amounts of these additives are usually small, they can play an important role in determining the quality of the final product. Light extrusion oils and lubricants, including petroleum oils, waxes, fatty acids, and esters, are often added to the mix to improve the extrusion rates and structure of the extruded products. Chemical inhibitors are introduced to reduce the detrimental effects of sulfur in high sulfur cokes. Iron oxide is often added to high sulfur coke to prevent puffing, the rapid swelling of the coke caused by volatilization of the sulfur at 1600–2400°C. The iron from Fe_2O_3 or other iron compounds prevents this action by forming a more stable iron sulfide, which reduces the gas pressure in the coke particles (44). Other sulfide-forming compounds such as those from sodium, nickel, cobalt, and vanadium may also be used.

3.4. Calcining. Nearly all raw coke utilized in carbon manufacture is calcined. Calcination consists of heating raw coke to remove volatiles and to shrink the coke to produce a strong, dense particle. Raw petroleum coke, eg, has 5–15% volatile matter. When the coke is calcined to 1400°C, it shrinks approximately 10–14%. Less than 0.5% of volatile matter in the form of hydrocarbons remains in raw coke after it is calcined to 1200–1400°C. During calcination, the evolving volatiles are primarily methane and hydrogen, which burn during the calcining process to provide much of the heat required. The calcining step is particularly important for those materials used in the manufacture of graphite products, such as electrodes, since the high shrinkages occurring in raw coke during the baking cycle of large electrodes would cause the electrode to crack. To prevent partial fusion of the coke during calcining, the volatile content of the green coke is kept below 12%. The real density of coke increases during calcining from about 1.3 g/mL to 2.0–2.2 g/mL.

Anthracite is calcined at appreciably higher temperatures (1800–2000°C). The higher calcining temperatures for anthracite are necessary to complete most of the shrinkage and to increase the electrical conductivity of the product for use

in either Soderberg or prebaked carbon electrodes for aluminum, silicon, or phosphorus manufacture.

The selection of calcining equipment depends on the temperatures required and the materials to be calcined. There are two principal types of coke calcining units in operation utilizing either kilns or hearths.

A calcining kiln is a horizontal steel cylinder, slightly sloped to help the coke move forward and lined with refractory brick. The raw coke is fed at the upper end, natural gas or oil is burned at the lower end, and the combustion gas flows through the kiln above and against the coke stream.

The rotary hearth is a horizontal plate, which is lined with refractory and turns at a slow rate. The coke enters at the perimeter and moves toward the center. Natural gas is fired around the circumference of the dome and the hot coke drops through a central pit into a rotary cooler.

The yield of coke calcined in a kiln is usually slightly above 80% of the dry raw coke. Higher yields are achieved in rotary hearths because very little of the fines are burned or carried away by the combustion gas.

Since anthracite must be calcined at higher temperatures than can be reasonably attained in conventional gas-fired kilns, an electrically heated shaft kiln is used to calcine coal at temperatures up to 2000°C (45).

4. Processing

4.1. Crushing and Sizing. Calcined petroleum coke arrives at the graphite manufacturer's plant in particle sizes ranging typically from dust to 50–80 mm diameter. In the first step of artificial graphite production, the run-of-kiln coke is crushed, sized, and milled to prepare it for the subsequent processing steps. The degree to which the coke is broken down depends on the grade of graphite to be made. If the product is to be a fine-grained variety for use in aerospace, metallurgical, or nuclear applications, the milling and pulverizing operations are used to produce sizes as small as a few micrometers in diameter. If, on the other hand, the product is to be coarse in character for products like graphite electrodes used in the manufacture of steel, a high yield of particles up to 25 mm diameter is necessary.

The wide variety of equipment available for the crushing and sizing operations is well described in the literature (46,47). Roll crushers are commonly used to reduce the incoming coke to particles that are classified in a screening operation. The crushed coke fraction, smaller than the smallest particle needed, is normally fed to a roll or hammer mill for further size reduction to the very fine (flour) portion of the carbon mix. A common flour sizing used in the graphite industry contains particles ranging from 149 μm (100 mesh) to a few micrometers with about 50% passing through a 74 μm (200 mesh) screen.

For a coarse-grained (particle containing) graphite, the system depicted in Figure 3 is typical. The run-of-kiln coke is brought in on railroad cars and emptied into pits where the coke is conveyed to an elevator. The elevator feeds a second conveyor that empties the coke into any one of a number of storage silos where the coke is kept dry. The manufacturer usually specifies a maximum

Fig. 3. Raw materials hand ling system. (Courtesy of UCAR Carbon Technology Corp.)

moisture content in the incoming coke at about 0.1–0.2% to ensure that mix compositions are not altered by fluctuations in moisture content.

In the system shown in Figure 3 the oversized coke particles (heads) are diverted to a roll crusher. Most raw material systems provide the option of further reducing the sizes of particles by passing them through a second crusher directly from the screens and recycling the resulting fractions through the screening system. The undersized coke fractions are transferred to a bin that supplies a mill for production of the flour portion of graphite composition. The mills used in this application may be of impact (hammer) variety or of roller variety. A commonly used mill consists of a rotating roller operating against a stationary steel ring. The coke is crushed to very fine sizes that are air-classified by a cyclone separator. The sizes larger than those desired in the flour are returned to the mill and the acceptable sizes are fed to a charge bin.

The coal-tar pitch binder used in graphite manufacture also arrives in railroad cars. If the pitch is shipped in bulk form, the large pieces must be crushed to ca 30 mm and smaller to facilitate uniform melting in the mixer and control of the weighing operation. Many vendors of binder pitches now form their product either by prilling, extruding, or flaking to ensure ease of handling and storage.

The pitch system shown in Figure 3 conveys the incoming pitch through a crusher to an elevator that deposits it into a charging bin. The graphite manufacturer tries to avoid long-term storage of 100°C softening point pitch because of its tendency to congeal at ambient conditions into masses extremely difficult to break up and handle. Thus, whenever possible, cars of pitch are ordered and used as needed at the carbon plant.

In some plants the pitches are received and stored as liquids. Addition to the mixers can be either through a weighing system or positive displacement pumps (48). Except for equipment differences, the results of utilizing liquid pitch are similar to bulk.

4.2. Proportioning. The size of the largest particle is generally set by application requirements. For example, if a smoothly machined surface with a minimum of pits is required, as in the case of graphites used in molds, a fine-grained mix containing particles no larger than 1.6 mm with a high flour content is ordinarily used. If high resistance to thermal shock is necessary, eg, in graphite electrodes used in melting and reducing operations in steel plants, particles up to 25 mm are used to act as stress absorbers in preventing catastrophic failures in the electrode.

Generally, the guiding principle in designing carbon mixes is the selection of the particle sizes, the flour content, and their relative proportions in such a way that the intergranular void space is minimized. If this condition is met, the volume remaining for binder pitch and the volatile matter generated in baking are also minimized. Volatile evolution is often responsible for structural and property deterioration in the graphite product. In practice, most carbon mixes are developed empirically with the aim of minimizing binder demand and making use of all the coke passed through the first step of the system. From an economic standpoint, accumulation of one size component cannot be tolerated in making mixes for commonly used graphite grades since this procedure amounts to a loss of relatively costly petroleum coke. Typically, a coarse-grained mix may contain a large particle, eg, 13 m diameter, two to three intermediate particle

sizes, and flour. In this formulation approximately 25 kg of binder pitch would be used for each 100 kg of coke.

Although binder levels increase as particle size is reduced, and they are greatest in all-flour mixes where surface area is very high, the principle of minimum binder level still applies. The application of particle packing theory to achieve minimum binder level in all-flour mixes is somewhat more complex because of the continuous gradation in sizes encountered (49).

For some carbon and graphite grades, particle packing and minimum pitch concepts are not used in arriving at a suitable mix design. For relatively small products, eg, where large dimensional changes can be tolerated during the baking and graphitizing operations, high binder contents are often used. Increased pitch content results in greater shrinkage, which gives rise to high density and strength in the finished products.

4.3. Mixing. Once the raw materials have been crushed, sized, and stored in charging bins and the desired proportions established, the manufacturing process begins with the mixing operation. The purpose of mixing is to blend the coke filler materials and distribute the pitch binder over the surfaces of the filler grains as it melts or is added as a liquid. The intergranular bond ultimately determines the properties and structural integrity of the graphite. Thus the more uniform the binder distribution is throughout the filler components, the greater the likelihood for a structurally sound product.

The degree to which mixing uniformity is accomplished depends on factors such as time, temperature, and batch size. However, a primary consideration in achieving mix uniformity is mix design (see MIXING AND BLENDING). A number of mechanically agitated, indirectly heated mixer types are available for this purpose (50,51). Each mixer type operates with a different mixing action and intensity. Ideally, the mixer best suited for a particular mix composition is one that introduces the most work per unit weight of mix without particle breakdown. In practice, only a few mixer types are used in graphite manufacture.

The cylinder mixer is commonly used for coarse-grained mixes. It is equipped with an axial rotating shaft fitted with several radial arms where paddles are attached. The intensity of this mixer is relatively low to avoid particle breakdown and long mixing times, such as 90 min, are therefore needed to complete the mixing operation. With fine-grained compositions, more intensive mixers may be used with a corresponding reduction in mixing time. Bread or sigma-blade mixers and the high intensity twin-screw mixers of the Werner-Pfleiderer and Banbury variety are examples of the equipment that can be used on fine-grained compositions. For both mixers temperatures at the time of discharge are 160–170°C.

Following the mixing operation, the hot mix must be cooled to a temperature slightly above the softening point of the binder pitch. Thus the mix achieves the proper rheological consistency for the forming operation and the formed article is able to maintain its shape better as it cools to room temperature. At the end of the cooling cycle, which typically requires 15–30 min, the mix is at 100–110°C and is ready to be charged into an extrusion press or mold.

4.4. Forming. One purpose of the forming operation is to compress the mix into a dense mass so that pitch-coated filler particles and flour are in intimate contact. For most applications, a primary goal in the production of graphite

is to maximize density; this goal begins by minimizing void volume in the formed, green, product. Another purpose of the forming step is to produce a shape and size as near that of the finished product as possible. This reduces raw material usage and cost of processing graphite that cannot be sold to the customer and must be removed by machining prior to shipment. Two important methods of forming are extrusion and molding.

Extrusion. This process is used to form most carbon and graphite products. In essence, extrusion presses comprise a removable die attached by means of an adapter to a hollow cylinder called a mud chamber. The cylinder is charged with mix that is extruded in a number of ways depending on the press design. For one type of press, the cooled mix is introduced into the mud chamber in the form of plugs that are molded in a separate operation. A second type of extruder called a tilting press makes use of a moveable mud chamber-die assembly to eliminate the need for precompacting the cooled mix. Loading occurs directly from coolers with the assembly in the vertical position; the mixture is extruded with the assembly in the horizontal position. A third type of extrusion press makes use of an auger to force mix through the die. This press is used principally with fine-grained mixes because of its tendency to break down large particles.

The basic steps in the extrusion operation when a tilting press is used are depicted in Figure 4. The cooled mix is usually fed to the press on a conveyor belt where it is discharged into the mud chamber in the vertical position. A ram descends on the filled chamber, tamping the mix to compact the charge. A closing plate located in the pit beneath the press is often used to seal off the die opening, thereby preventing the mix from extruding during the application of high tamping pressures. In addition, a vacuum can be applied to the mud chamber during

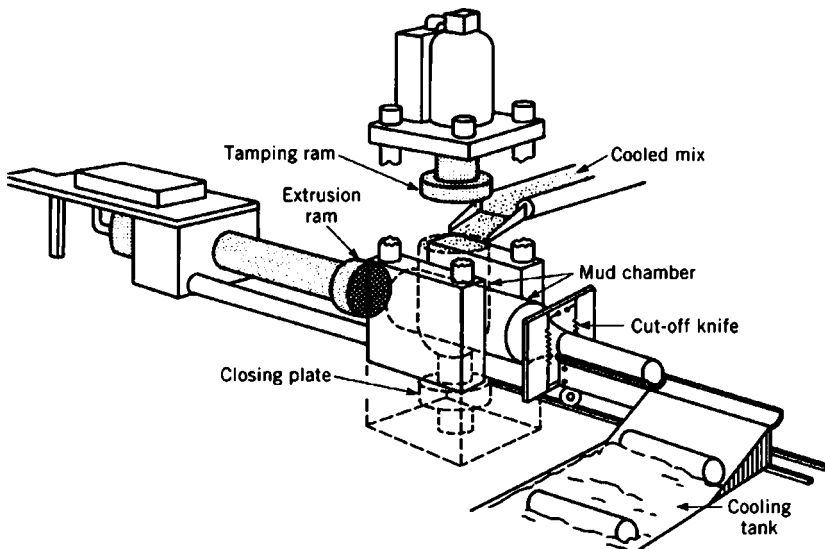


Fig. 4. Tilting extrusion press. (Courtesy of UCAR Carbon Technology Corp.)

tamping to remove entrapped air. The filling and tamping procedures are repeated until the mud chamber is filled with tamped mix and then rotated back to the horizontal position. The extrusion ram then enters the mud cylinder forcing the mix through the die at 3–15 MPa (30–148 atm). A guillotinellike knife located near the die outlet cuts the extruded stock to the desired length. Round products are rolled into a tank of water where the outer portions are quickly cooled to prevent distortion of the plastic mass. Products having large rectangular cross-sections may be transferred from the press to the cooling tank by means of an overhead crane. Water temperatures are regulated to avoid cracking as a result of too rapid cooling. Products with smaller cross-sections, such as $32 \times 152 \times 810$ mm plates used as anodes, may be cooled in air on steel tables. Bulk densities of green products range typically from 1.75–1.80 g/cm³.

The anisotropy, usually observed in graphite products, is established in the forming operation. In extruded products, the anisotropic coke particles orient with their long dimensions parallel to the extrusion direction. The layer planes of the graphite crystals are predominantly parallel to the long dimension of the coke particle. Accordingly, the highly anisotropic properties of the single crystal are translated, to a greater or lesser degree depending on several factors, to the graphite product. The most important of these factors are coke type, particle size, and the ratio of die-to-mud chamber diameters. The more needlelike the coke particle, the greater the difference is between properties with-grain (parallel to the extrusion direction) and cross-grain. The use of smaller particles in the mix design also increases this property difference; the presence of large particles interferes with the alignment process. As the ratio of mud cylinder-to-die diameter increases, the with-grain to cross-grain ratios of strength and conductivity increase, whereas the with-grain to cross-grain ratios of resistivity and expansion coefficient decrease. Thus anisotropy is increased for the same coke type and mix design when going from a 600 mm diameter die to a 400 mm diameter die on the same extrusion press. As a result of particle orientation in extruded graphitized products, strength, Young's modulus, and thermal conductivity values are greater; whereas, electrical resistivity and coefficient of thermal expansion are smaller in the with-grain direction than in the two cross-grain directions.

Molding. Molding is the older of the two forming methods and is used to form products ranging in size from brushes for motors and generators to billets as large as 1.75 m diameter by 1.9 m in length for use in specialty applications.

Several press types are used in molding carbon products. The presses may be single-acting or double-acting, depending on whether one or both platens move to apply pressure to the mix through punched holes in either end of the mold. The use of single-acting presses is reserved for products whose thicknesses are small compared with their cross-sections. As thickness increases, the acting pressure on the mix diminishes with distance from the punch because of frictional losses along the mold wall. Acceptable thicknesses of molded products can be increased by using double-acting presses that apply pressures equally at the top and bottom of the product.

Jar molding is another method used to increase the length of the molded piece and keep nonuniformity within acceptable limits. By this technique, the heated mold is vibrated as the hot mix is introduced, thus compacting the mix

during the charging operation. Pieces as large as 2.5 m in diameter and 1.8 m in length have been molded in this way; the green densities are comparable with those obtained in extruded materials.

Smaller products, such as brushes and seal rings, are often molded at room temperature from mix that is milled after cooling. When binder levels exceed approximately 30% of the mix, the compacted milled mix has sufficient green strength to facilitate handling in preparation for the baking operation.

In a typical hot molding operation to form a 1.7 m diameter billet 1.3 m long, approximately 7200 kg of mix at 160°C is introduced into a steam heated mold without cooling. The platens of the press compact the mix at ca 5 MPa (49 atm), holding this pressure for 15–30 min. The cooling step for pieces of this size is the most critical part of the forming operation. Owing to the low thermal conductivity of pitch, 0.13 W/(m·K) (52), and its relatively high expansion coefficient at 25–200°C ($4.5 \times 10^{-4}/^{\circ}\text{C}$) (53), stresses build rapidly as the outer portions of the piece solidify. If cooling is too rapid, internal cracks are formed that are not removed in subsequent processing steps. As a result, a cooling schedule is established for each product size and is carefully followed by circulating water of various temperatures through the mold for specified time periods. When the outside of the piece has cooled sufficiently, it is stripped from the mold and the cooling operation continued by direct water spray for several hours. If cooling is stopped too soon, heat from the center of the piece warms the pitch binder to a plastic state, resulting in slumping and distortion. The cooled piece is usually stored indoors prior to baking in order to avoid extreme temperature changes that may result in temperature gradients and damage to the structure. Bulk density of the green billet is usually 1.65–1.70 g/cm³.

As with extruded products, molded pieces have a preferred grain orientation. The coke particles are aligned with their long dimensions normal to the molding direction. Thus the molded product has two with-grain directions and one cross-grain direction which coincides with the molding direction. Strength, modulus, and conductivity of molded graphites are higher in both with-grain directions and expansion coefficient is higher in the cross-grain direction. Isostatic molding is a forming technique used to orient the coke filler particles randomly, thereby imparting isotropic properties to the finished graphite. One approach to isostatic molding involves placing the mix or blend into a rubber container capable of withstanding relatively high molding temperatures. The container is evacuated then sealed and placed in an autoclave that is closed and filled with heated oil. The oil is then pressurized to compact the mass, which may then be processed in the usual way to obtain isotropic graphite. Cold isostatic molding is also used. In this process, room temperature water fills the autoclave and is pressurized to compact the mass.

4.5. Baking. In the next stage, the baking operation, the product is fired to 800–1000°C. One function of this step is to convert the thermoplastic pitch binder to solid coke. Another function of baking is to remove most of the shrinkage in the product associated with pyrolysis of the pitch binder at a slow heating rate. This procedure avoids cracking during subsequent graphitization where very fast firing rates are used. The conversion of pitch to coke is accompanied by marked physical and chemical changes in the binder phase, which if

conducted too rapidly, can lead to serious quality deficiencies in the finished product. For this reason, baking is generally regarded as the most critical operation in the production of carbon and graphite.

Several studies discuss the kinetics of pitch pyrolysis and indicate, in detail weight loss and volatile evolution as functions of temperature (54,55). Weight losses of 30–40% occur, indicating that for every 500 kg of green product containing 20% pitch, 30–40 kg of gas must escape. In terms of gas volume, approximately 150 cm³ of volatiles at standard conditions must be evolved per gram of pitch binder during the baking operation. The product in the green state is virtually impermeable, and the development of a venting porosity early in the bake must be gradual to avoid a grossly porous or cracked structure. The generation of uniform structure during the bake is made more difficult by the poor thermal conductivity of pitch. Long firing times are usually needed to drive the heat into the center of the product, which is necessary for pitch pyrolysis and shrinkage. If the heating rates exceed a value which is critical for the size and composition of the product, differential shrinkage leads to splitting. Shrinkage during baking is of the order of 5% and increases with increasing pitch content. Added to these difficulties is the complete loss of mechanical strength experienced by the product in the 200–400°C range where the pitch binder is in a liquid state. To prevent slumping and distortion during this period, the stock must be packed in carefully sized coke or sand, which provides the necessary support and is sufficiently permeable to vent the pitch volatiles.

A variety of baking furnaces are in use to provide the flexibility needed to bake a wide range of product sizes and to generate the best possible temperature control. One common baking facility is the pit furnace, so named because it is positioned totally or partially below ground level to facilitate improved insulation. In essence, the pit furnace is a box with ceramic brick walls containing ports of flues through which hot gases are circulated. Traditionally, natural gas has been the fuel used to fire pit furnaces; however, pit furnaces can also be converted to use fuel oil (see FURNACES, FUEL-FIRED).

Another common baking facility is the so-called ring furnace; one form of this is depicted in Figure 5. Two equal rows of pit furnaces are arranged in a rectangular ring. Ports in the furnace walls permit the heated gases from one furnace to pass to the next until the cooled gases are exhausted by a movable fan to a flue leading to a stack. A movable burner, in this case located above one furnace, fires it to a predetermined off-fire temperature. The firing time per furnace is 18–24 h. When the desired temperature has been reached, the burner is moved to the adjacent furnace which has been heated by gases from the most recently fired pit. At the same time, the fan is moved to a furnace that has just been packed. This process continues, with packing, unloading, and cooling stages separating the fan and the burner. Cycle times in this furnace are three to four weeks. Thermally, the ring furnace is highly efficient but it has the disadvantage that very little control can be exercised over heating rates.

A more recent development is the carbottom furnace, which is an above ground rectangular kiln; the bottom is mounted on wheels and set on tracks so it is movable. The carbottom is isolated from the heating chamber by a water seal. These furnaces provide improved temperature and pressure control and better uniformity.

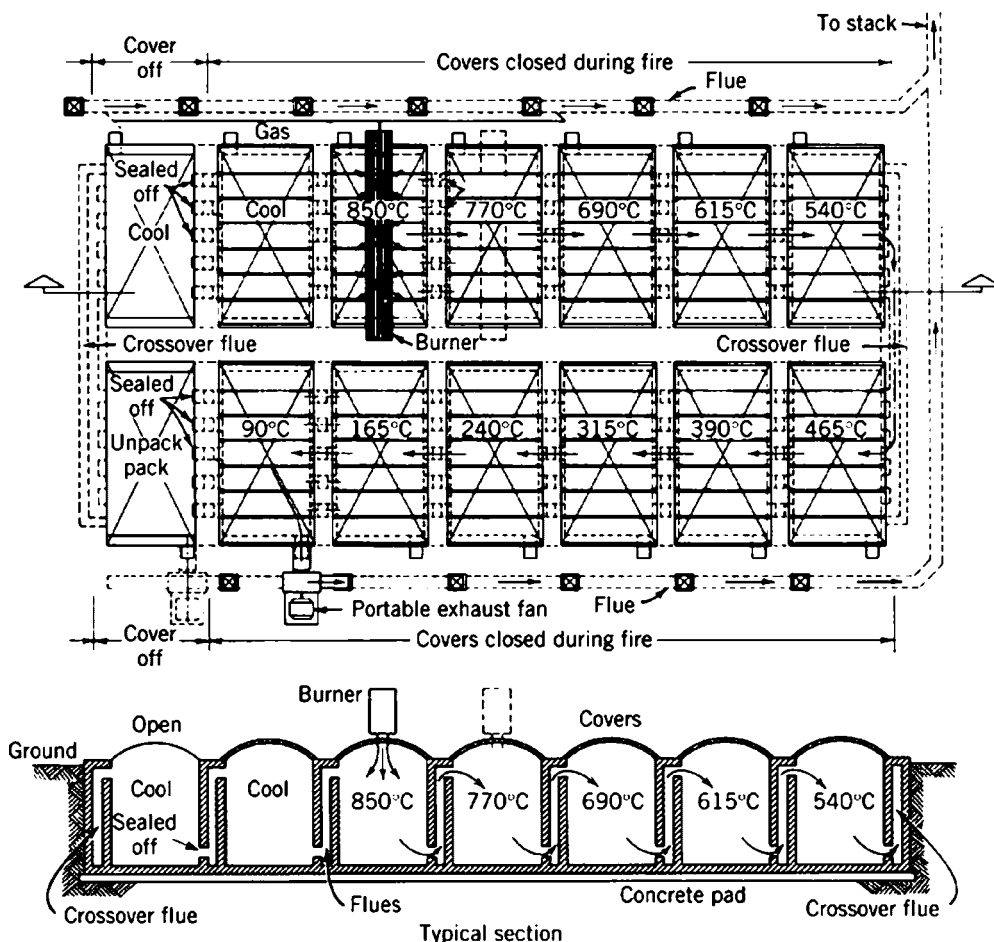


Fig. 5. Ring furnace system. (Courtesy of UCAR Carbon Technology Corp.)

In addition, the development of stainless steel cans, saggars, into which green stock is loaded and then surrounded by packing media, has improved furnace heating effectiveness by reducing the ratio of packing media to green electrode. The can diameter is slightly larger than the stock diameter to accommodate this process. Beside reducing total energy requirements as much as 60–70%, the sagger allows the use of automated equipment in loading, unloading, and handling of the electrodes (56).

The firing schedules used in the baking operation vary with furnace type, product size, and binder content. A bulk furnace packed with $610 \times 810 \times 4600$ mm pieces of specialty graphite may require six weeks to fire and an additional three to four weeks to cool. In contrast, very small products, such as seal rings, may be baked in tunnel kilns in a few hours. A sagger furnace containing electrodes may require 12–14 days to reach final temperature with an additional 3–5 days to cool. Firing rates early in the baking schedule are reduced to permit

pitch volatiles to escape slowly, minimizing damage to the structure. For most carbon products, temperatures must be well below 400°C prior to unpacking to avoid cracking because of thermal shock. The product is scraped or sanded to remove adhering packing materials and is then weighed, measured, and inspected prior to being stored for subsequent processing. Some products that are sold in the baked state are machined at this stage. Baked products include submerged arc-furnace electrodes, cathode blocks for the electrolytic production of aluminum, and blast furnace lining blocks.

4.6. Impregnation. In some applications, the baked product is taken directly to the graphitizing facility for heat treatment to 3000°C. However, for many high performance applications of graphite, the properties of stock processed in this way are inadequate. The method used to improve those properties is impregnation with coal-tar or petroleum pitches. The function of the impregnation step is to deposit additional pitch coke in the open pores of the baked stock, thereby improving properties of the graphite product. Table 6 shows the graphite properties of unimpregnated and impregnated stock 150–300 mm diameter and containing 1.5 mm particles as the largest particle.

Further property improvements result from additional impregnation steps separated by rebaking operations. However, the gains realized diminish quickly, for the quantity of pitch picked up in each succeeding impregnation is approximately half of that in the preceding treatment. Many nuclear and aerospace graphites are multiple pitch-treated to achieve the greatest possible assurance of high performance.

During the baking operation, binder pitch exuding the product surface creates a dense impermeable skin. In addition, the exuding pitch causes packing material to adhere to the baked stock. The skin and the packing material must be removed by sanding, scraping, or machining before the stock can be impregnated on a reasonable time cycle. Unless this operation is properly performed,

Table 6. Effect of One Pitch Impregnation on Graphite Properties

Property	Unimpregnated ^a		Impregnated ^b	
	wg ^c	ag ^d	wg ^c	ag ^d
Young's modulus, GPa ^e	7.4	4.4	11.0	6.3
flexural strength, MPa ^f	10.	7.1	17	13
tensile strength, MPa ^f	5	4.4	8.1	7.3
compressive strength, MPa ^f	21	21	34	33
permeability, μm^{2g}	0.39	0.35	0.19	0.16
coefficient of thermal expansion, $10^{-6}/^{\circ}\text{C}$	1.3	2.7	1.5	3.1
specific resistance, $\mu\Omega \cdot \text{m}$	8.8	13.0	7.6	11.0

^aBulk density = 1.6 g/mL.

^bBulk density = 1.7 g/mL.

^cWith the grain, ie, samples cut parallel to the molding plane or extrusion axis.

^dAcross the grain, ie, samples cut perpendicular to the molding or extrusion force.

^eTo convert GPa to psi, multiply by 145,000.

^fTo convert MPa to psi, multiply by 145.

^gTo convert μm^2 to darcys, divide by 0.9869.

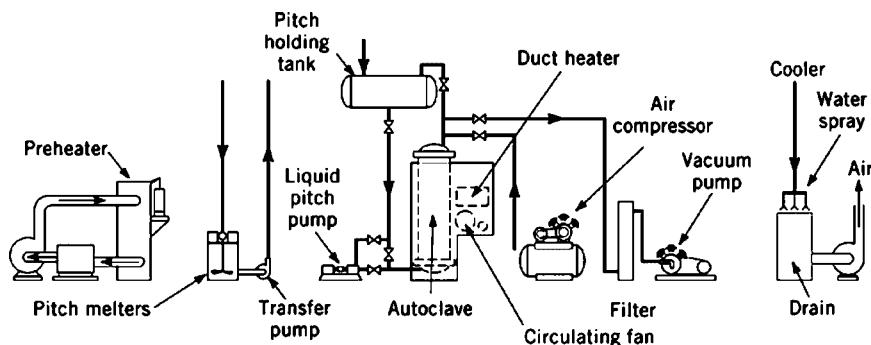


Fig. 6. Pitch impregnation system. Courtesy of UCAR Carbon Technology Corp.

the impregnant may not reach the center of the product and a so-called dry core results. When this condition exists, the product usually splits during graphitization as a consequence of the greater concentration of pitch and greater shrinkage in the outer portions of the stock. The likelihood of a dry core increases with the quinoline-insoluble solids content of the impregnant. During the impregnation process, the insolubles form a filter cake of low permeability on the stock surface, reducing the penetrability of the impregnant. Quinoline insolubles significantly greater than 5% reduce the penetration rate and increase the incidence of dry cores.

A schematic diagram of the pitch impregnation process is shown in Figure 6. Before it is placed in an autoclave, the skinned baked stock is preheated to 250–300°C to thoroughly dry it and to facilitate free flow of the molten impregnant into the open pores. The first step in the impregnation process is to evacuate the stock to pressures below 3.5 kPa (26 mm Hg) for a period of one hour or more depending on the size and permeability of the stock. Unless the stock is adequately evacuated, the remaining air prevents thorough penetration of the impregnant to the center of the product. Heated pitch is then introduced by gravity flow into the autoclave from a holding tank until the charge is completely immersed. The system is then subjected to pressures of 700–1500 kPa ($\sim 7 - 15$ atm) for several hours to shorten the time for pitch penetration. When the pressure cycle has been completed, the pitch is blown back to the holding tank by means of compressed air. The autoclave is then opened, and the stock is transferred to a cooler where water and/or circulating air accelerate the cooling process. After cooling, the stock is weighed to determine the quantity of pitch picked up. If the pickup is below a specified limit, the stock is scrapped. Depending on the density of the baked stock, the pickup is 12–16% on the first impregnation and 6–8% on the second impregnation.

If the stock is to receive a second impregnation, it must be rebaked. In the past, stock containing raw impregnating pitch could be graphitized directly. However, the air polluting effect caused by this practice has made rebaking a necessary preliminary step to graphitization in order to achieve effective environmental control.

4.7. Graphitization. Graphitization is an electrical heat treatment of the product to ca 3000°C. The purpose of this step is to cause the carbon atoms

in the petroleum coke filler and pitch coke binder to orient into the graphite lattice configuration. This ordering process produces graphite with intermetallic properties that make it useful in many applications.

Very early in the carbonization of coker feeds and pitch, the carbon atoms are present in distorted layers of condensed benzene ring systems formed by the polymerization of the aromatic hydrocarbons in these materials. X-ray studies of raw coke, for example, show two-dimensional order at that early stage of graphite development (57). As the temperature of coke increases, the stack height of the layer plane increases. The layers are skewed about an axis normal to them, however, and it is not until a temperature of ca 2200°C is reached that three-dimensional order is developed. As the graphitizing temperature is increased to 3000°C, the turbostratic arrangement of the layer planes is effectively eliminated, and the arrangement of the carbon atoms approaches that of the perfect graphite crystal. Depending on the size and orientation of these crystals, the properties of manufactured graphites can be varied controllably to suit a number of critical applications.

The furnace that made the graphite industry possible was invented in 1895 by Acheson (58) and is still in use today with only minor modifications. It is an electrically fired furnace capable of heating tons of charge to temperatures approaching 3000°C. The basic elements of the Acheson furnace are shown in Figure 7. The furnace bed is made up of refractory tiles supported by concrete

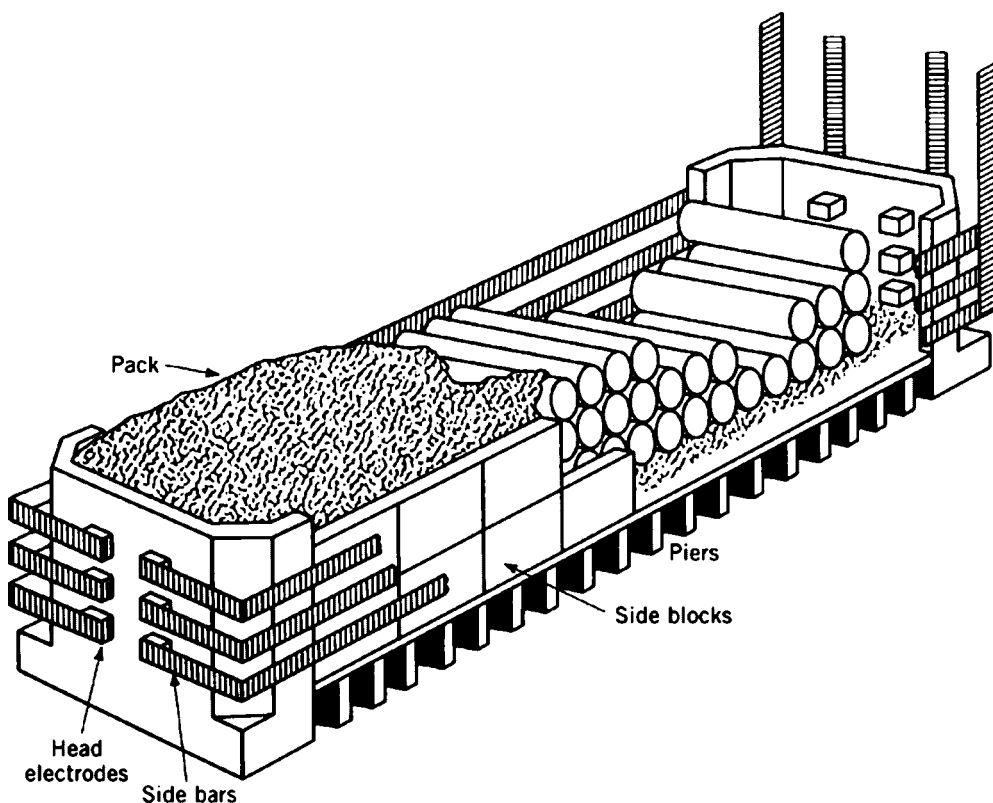


Fig. 7. The Acheson furnace. Courtesy of UCAR Carbon Technology Corp.

piers. The furnace ends are U-shaped concrete heads through which several graphite electrodes project into the pack. These electrodes, which are water-cooled during operation, are connected by copper bus work to the secondary of a transformer. The product is placed on a layer of metallurgical coke with its long axis transverse to current flow. Although a cylindrical product is shown in Figure 7, any product shape can be graphitized in the Acheson furnace so long as the product pieces are carefully spaced. This feature of the Acheson furnace makes it extremely versatile. The spacing between pieces may vary from less than a centimeter to several centimeters, depending on the shape and size of the product. With the product in place, a coarsely sized metallurgical coke, called resistor pack, is used to fill the interstices between pieces; most of the heat needed to reach graphitizing temperatures is generated in the resistor material. Once the charge and resistor material are loaded, the furnace is covered with a finer blend of metallurgical coke, sand, and silicon carbide to provide thermal and electrical insulation. Concrete side blocks, usually 0.5–1 m from the charge ends, are used to retain the insulation. The procedure for loading a furnace usually requires one day.

Acheson furnace sizes may vary, depending on the product size and the production rate desired. Typically, the furnace may be 12–15 m by 3–3.5 m. Loads ranging from 35–55 metric tons of product are charged to these furnaces. The transformers used are rated 4000–6000 kW and are capable of delivering up to 60,000 A to the charge. Heating rates are usually 40–60°C/h; the total firing time is approximately three days. At the end of this time, the product temperatures are 2800–3000°C. Total power input varies, depending on the product and load size; for graphite electrodes, total power (energy) inputs average 4.5 kW · h/kg, and total power inputs in excess of 9 kW · h/kg may be used in the thermal purification of nuclear graphites. Following the heating cycle, 8–10 days are needed to cool and unload the furnace. The total cycle time on an Acheson furnace is ca two weeks. The cooling procedure is hastened by the gradual removal of pack with care to leave sufficient cover to prevent oxidation of the product. The insulation and resistor materials are screened to specified sizes and proportions for reuse; new materials are added as necessary. The product is cleaned and inspected prior to being measured and weighed for bulk density and resistivity determinations. If the properties are within specified limits, the product is stored and is ready for machining.

Furnaces other than the Acheson furnace are used commercially but on a much smaller scale and usually for smaller products. For example, electrographitic brushes are graphitized in tube furnaces, wherein a current-carrying graphite tube is the heating element. These furnaces are particularly useful in the laboratory because of the ease with which they can be loaded and unloaded without the need for handling large quantities of packing material. Inductively-heated furnaces are also used commercially to graphitize a limited number of products, such as some aerospace grades and carbon fibers. These furnaces, also popular in the laboratory, consist basically of a cylindrical graphite shell susceptor positioned inside a water-cooled copper coil. High frequency power supplied to the coil induces current to flow in the susceptor, heating it and causing it to radiate heat to the contained charge (see FURNACES, ELECTRIC).

Several patents (59–63) have been issued describing a process for graphitization where the carbon charge to be heated is placed in a longitudinal array and

covered with insulation to prevent heat losses and oxidation of the charge. An electric current is passed directly through the carbon array, generating within the carbon the heat required to raise the carbon to the graphitization temperatures. These furnaces, because of the direct heating of the carbon charge, utilize less than $4.4 \text{ kW} \cdot \text{h/kg}$ and can be cycled from load-to-reload in less than a week (56).

4.8. Puffing. In the temperature range of $1500\text{--}2000^\circ\text{C}$, most petroleum cokes and coal-tar pitch cokes undergo an irreversible volume increase known as puffing. This effect in petroleum cokes has been associated with thermal removal of sulfur and increases with increasing sulfur content. Some mechanisms other than sulfur removal may be more dominant in coal-tar pitch cokes. Because of the recent emphasis on the use of low sulfur fuels, many of the sweet crudes that had been used to produce coker feedstocks are now being processed as fuels. Desulfurization of sour crudes or coker feeds is possible but expensive. The result is an upward trend in the sulfur content of many petroleum cokes, leading to greater criticality in heating rate in the puffing temperature range during graphitization.

Many studies of the puffing phenomenon and of means for reducing or eliminating it have been made (64–67). As a general rule, puffing increases as particle size increases and is greater across the product grain. Depending on particle size and on the product size, heating rates must be adjusted in the puffing range to avoid splitting the product. Fortunately, the use of puffing inhibitors has eased the problem and has permitted the use of graphitization rates greater than would otherwise be possible.

5. Uses

5.1. Aerospace and Nuclear Reactor Applications. Graphite with its exceptional strength and thermal stability at high temperatures is a prime candidate material for many aerospace and nuclear applications. Its properties, through process modifications, are tailorable to meet an array of design criteria for survival under extremely harsh environmental operations.

Graphite is a lightweight structural material that retains most of its mechanical strength even at temperatures in excess of 2200°C . It has a high resistance to thermal shock and exhibits good neutron interaction characteristics and stability under irradiation. The ease of machining and commercial availability of graphite are other desirable qualities for these applications; however, oxidation at high temperatures presents a problem requiring oxygen protective systems for any prolonged use.

Aerospace and nuclear reactor applications of graphite demand high reliability and reproducibility of properties, physical integrity of product, and product uniformity. The manufacturing processes require significant additional quality assurance steps that result in high cost.

Aerospace. Graphite applications in the aerospace industry include rocket nozzle components, nose cones, motor cases, leading edges, control vanes, blast tubes, exit cones, thermal insulation, and any other applications where a rapid temperature rise and unusually high operating temperatures are encountered.

Graphite is one of the few materials that can reasonably meet the demands encountered under these conditions. Of particular importance in this type of application are the excellent thermal properties of graphite, eg, high thermal shock resistance, high thermal stress resistance, and a strength increase with temperature increase. In addition, its excellent machinability makes it possible to maintain the required close tolerances for the machining of precision components for aerospace vehicles.

The erosion of graphite in nozzle applications is a result of both chemical and mechanical factors. Changes in temperature, pressure, or fuel-oxidizing ratio markedly affect erosion rates. Graphite properties affecting its resistance to erosion include density, porosity, and pore size distribution (see ABLATIVE MATERIALS).

The entrance cap, throat, and exit cone sections in a typical nozzle are frequently made or lined with conventional bulk graphite, especially in small nozzles where dimensional stability is extremely important, since a small change in dimension causes a relatively large change in performance. In other designs the throat may be made of conventional graphite with entrance cap and exit cone molded of carbon or graphite fibrous materials that serve as reinforcement for high temperature plastic materials. In larger nozzles, all three sections might be made of fiber-reinforced material because of high strength, light weight, and ease of construction of the composite materials.

Nose cones and leading edge components fabricated of graphite are used on both ballistic and glider-type reentry vehicles. Ballistic vehicles are exposed to short duration, extremely severe friction heating and oxidizing conditions upon reentry to the atmosphere. Glider-type reentry vehicles are exposed to less severe conditions for longer periods. Design technology and the ability to control properties of manufactured graphite favorably has increased its use in aerospace applications.

The severe operational environment of advanced high performance missiles and space vehicles imposes exacting requirements on structural components that must withstand temperatures of approximately 2000°C in oxidizing atmospheres. Extensive studies on coatings for the protection of graphite under these conditions has been carried out under U.S. Air Force funding (68). A thin coating of iridium metal (69) was found to be the only material that was totally satisfactory for the protection of graphite from oxidation at 2000°C.

Nuclear Applications. The strength of graphite at high temperatures and its behavior with respect to products of nuclear fission/fusion make it a suitable material for nuclear moderators and reflectors, materials of construction, and thermal columns in various reactors. Since its use in the first nuclear reactor, CP-1, constructed in 1942 at Stagg Field, University of Chicago, many thousands of metric tons of graphite have been used for this purpose. Uranium-graphite moderators were used in the Calder Hall reactors for power generation. The advanced gas-cooled reactors (AGR), the high temperature gas-cooled reactors (HTGR), the molten salt breeder reactors (MSBR), and liquid metal fueled reactors (LMFR) all use graphite moderators. The thermal stability, resistance to corrosion, and high thermal conductivity of graphite make it a most suitable moderator material for consideration in advanced design, high temperature, atomic energy efficient nuclear reactors.

Graphite is chosen for use in nuclear reactors because it is the most readily available material with good moderating properties and a low neutron capture cross section. Other features that make its use widespread are its low cost, stability at elevated temperatures in atmospheres free of oxygen and water vapor, good heat transfer characteristics, good mechanical and structural properties, and excellent machinability.

Neutron economy in graphite occurs because pure graphite has a neutron capture cross section of only $0.0032 \pm 0.002 \times 10^{-24} \text{ cm}^2$. Taking into account the density of reactor grade graphite (bulk density 1.71 g/cm^3), the bulk neutron absorption coefficient is $0.0003/\text{cm}$. Thus a slow neutron may travel $>32 \text{ m}$ in graphite without capture.

The purity of reactor-grade graphite is controlled by raw material selection and subsequent processing and purification. High temperature purification is used for most applications; however, some moderator graphites applications require considerably higher purity levels such as halogen purification to remove extremely stable carbides, especially that of boron. The actual purity requirements are determined by the reactor design.

On exposure to high temperature radiation (70) over a long period of time, graphite undergoes dimensional changes. For example, graphite initially contracts on exposure to fast neutron doses, but the rate of contraction decreases with exposure until it reaches a minimum volume; further exposure causes volume expansion, with the rate of expansion increasing rapidly at neutron

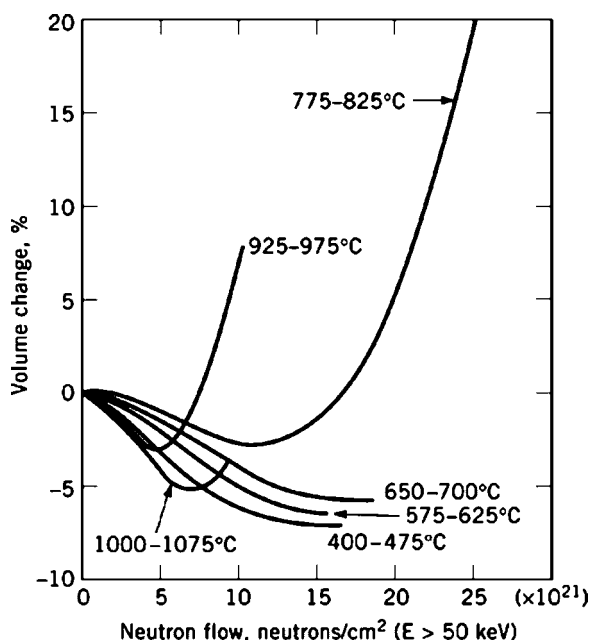


Fig. 8. Volume change in anisotropic graphite during General Electric Test Reactor (GETR) irradiations. Courtesy of Oak Ridge National Laboratory, managed by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy under Contract No. DE-AC05-84OR21400.

doses above 3×10^{22} neutrons/cm² (>50 keV) in all bulk graphite tested to date. This behavior is caused by atomic displacements that take place when graphite is exposed to fast neutrons, resulting in anisotropic crystallite growth rates. The crystal expands in the *c*-axis direction and contracts in the *a*-axis directions. The bulk dimensional change depends on the geometrical summation of the individual crystallite changes and, hence, is dependent on the starting materials and the method of fabrication. The extent of radiation damage is also strongly dependent on the temperature of the graphite during irradiation. The severity of graphite radiation damage at high temperatures was underestimated since the magnitude of this temperature dependence was not recognized until about 1965.

Figure 8 shows the volume change in a conventional nuclear graphite during irradiations at various temperatures of relatively high fluxes. Figure 9 shows the length change in an isotropic nuclear graphite during irradiations at various temperatures at relatively high fluxes. The actual changes in dimensions are, of course, different from grade to grade and depend largely on the degree of anisotropy present in the graphite. (70). A process for the treatment of radioactive graphite has been described (71).

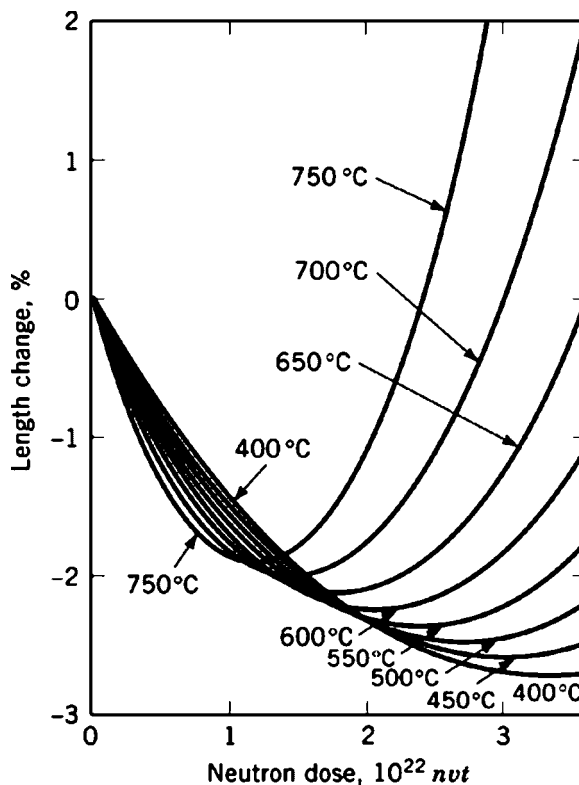


Fig. 9. Radiation-induced dimensional changes in isotropic graphite at various temperatures. nvt = neutron(density)·velocity·time. (Courtesy of Oak Ridge National Laboratory, managed by Martin Marietta Energy Systems, Inc. For the U.S. Department of Energy under Contract No. DE-AC05-84OR21400.)

Table 7. Properties of Nuclear Graphites^a

Property	Anisotropic graphite ^a	Isotropic graphite ^b
density, g/cm ³	1.71	1.86
resistance, $\mu\Omega \cdot \text{cm}$	735	1000
tensile strength, kPa ^{cb}	9,930	46,172
coefficient of thermal expansion (CTE), $10^{-6}/^{\circ}\text{C}$		
with-grain	2.2	5.3
against-grain	3.8	5.3
anisotropy ratio (CTE ratio)	1.73	1.0
total ash, ppm	740	400
boron content, ppm	0.4	0.3

^aRef. 72.^bRef. 5.^cTo convert kPa to psi, multiply by 0.145.

Table 7 (72) lists some useful properties of several graphites used for moderators or reflectors in nuclear reactors. Reactor designers have taken advantage of graphite's properties in applying the material to other than moderator and reflector components, usually in conjunction with some other material.

Combined as an admixture with some forms of boron or other high neutron absorbing elements, graphite offers advantages as a neutron shield, control rod, or secondary shutdown material of high temperature stability, without danger of meltdown. In fast reactors, where high energy neutrons reach the shield region, the presence of carbon atoms slows these neutrons down to energies where the probability of capture in the neutron absorber greatly increases. Graphite also serves as a stable matrix for the neutron absorber because it is able to withstand neutron and localized alpha recoil damage, offering protection against gross shield degradation.

Bulk graphites are also used in the HTGR concept to support and surround the active fuel core. These components tend to be large, complex-shaped blocks and have been produced from commercial grades of molded or extruded graphites.

In combination with compounds of uranium or thorium, graphite offers advantages as a matrix for fissile or fertile reactor fuel in thermal reactors. In this instance, the graphite serves a dual purpose, as a moderator and as a stable discharging phase for fuel. Its stability under irradiation and at high temperature aids in minimizing fuel degradation and permits longer useful fuel life. Because of its excellent thermal properties and mechanical integrity, graphite offers an excellent heat-transfer medium for heat removal and also resists thermal shock.

5.2. Chemical Applications. Carbon and graphite exhibit excellent resistance to the corrosive actions of acids, alkalies, and organic and inorganic compounds, an attribute that has fostered the use of graphite in process equipment where corrosion is a problem. Other than in the chemical process industries, graphite is used extensively in the steel, food, petroleum, pharmaceutical, and metal finishing industries. The high thermal conductivity and thermal stability of graphite have made it a useful material in heat exchangers and high temperature gas-spray coolers.

Manufactured carbon and graphite exhibit varying degrees of porosity depending on its method of preparation. Equipment fabricated from these materials must be operated essentially at atmospheric pressure; otherwise, some degree of leakage must be tolerated. Carbon used as a liner for tanks and vessels for the handling of highly corrosive inorganic acids such as hydrofluoric, nitric, phosphoric, sulfuric, and hydrochloric (73) is backed up by an impervious membrane of lead (74) or plastic to prevent seepage through the lining. The carbon lining protects the impermeable membrane material from adverse temperature and abrasion effects. Carbon linings have provided indefinite life with a minimum of maintenance.

Self-Supporting Structures. Self-supporting structures of carbon and graphite are used in a variety of ways. Water-cooled graphite towers serve as chambers for the burning of phosphorus in air. The high thermal conductivity of graphite allows rapid heat transfer to a water film on the outside of the tower, thereby maintaining inside wall temperature below 500°C, the oxidation temperature threshold of graphite. Phosphorus combustion chambers six meters in diameter by eleven meters in height (75) have been built using cemented graphite block construction.

The resistance of graphite to thermal shock, its stability at high temperatures, and its resistance to corrosion permit its use as self-supporting vessels to contain reactions at elevated temperatures (800–1700°C), eg, self-supporting reaction vessels for the direct chlorination of metal and alkaline-earth oxides. The vulnerability of cemented joints in these applications requires close tolerance (± 0.10 mm) machining, a feat easily accomplished on graphite with conventional metal machining equipment.

Carbon Raschig-ring tower packing is available in sizes of 10–77 mm diameter. Bubble-cap trays, up to 3 m diameter for hydrochloric–organic stripping towers, and packing support structures, up to 5.5 m diameter for scrubbing towers in pulp and paper mill liquor recovery processes, have been installed. Because none of these components requires complex machining or a high degree of imperviousness, carbon rather than graphite is often used in these applications because of its lower cost.

Impervious Graphite. For applications where fluids under pressure must be retained, impregnated materials are available (73). Imperviousness is attained by blocking the pores of the graphite or carbon material with thermosetting resins such as phenolics, furans, and epoxies. Because the resin pickup is relatively small (usually 12–15 wt%), the physical properties exhibited by the original graphite or carbon material are retained. However, the flexural and compressive strengths are usually doubled. Graphite is also made impervious in a vacuum impregnation process.

Because carbon is difficult to machine, very little impervious carbon equipment is made. However, impervious graphite has been accepted as a standard material of construction by the chemical process industry for the fabrication of process equipment, such as heat exchangers, pumps, valves, towers, pipe, and fittings (76,77).

Many types of impervious graphite shell and tube, cascade, and immersion heat exchangers are in service throughout the world (78). The most common is the shell and tube design where an impervious graphite tube bundle with fixed

and floating covers is employed in combination with a steel shell. Whenever parts must be joined, such as the tube to the tube sheet in a shell and tube heat exchanger, very thin resin cement joints are used. These resin cements have the same corrosion-resistant characteristics as the resins used to impregnate the graphite. Because of the high thermal conductivity of graphite, heat exchangers fabricated of impervious graphite have thermal efficiencies equal to metal heat exchangers of equivalent heat-transfer area. Heat exchangers up to 1.8 m diameter with areas up to 1300 m² are commercially available with operating pressures to 690 kPa (100 psi) and temperatures up to 170°C (79–81) (see HEAT EXCHANGE TECHNOLOGY).

Impervious graphite shells and tubes are used in numerous applications for transferring thermal energy, for example, boiling, cooling, or condensing. Large units are used extensively for cooling–condensing wet sulfur dioxide gas in sulfuric acid production plants that burn sludge acid (74).

Graphite heat exchangers are also used for evaporation of phosphoric acid and rayon spin bath solution; cooling electrolytic copper cell liquor; heating pickle liquor used for descaling sheet steel; boiling, heating, cooling, and absorbing hydrochloric acid and hydrogen chloride; and in many heating and cooling applications involving chlorinated hydrocarbons and sulfuric acid.

Impervious graphite heat exchangers machined from solid blocks are also available (82,83). The solid block construction is less susceptible to damage by mechanical shock, such as steam and water hammer, than are shell and tube exchangers. Block exchangers are limited in size and cost from 50–100% more than shell and tube units on an equivalent area basis.

Impervious graphite centrifugal pumps, pipe fittings, and valves were developed because most chemical processes require the movement of liquids. Graphite pipe and fittings in sizes ranging from 25 to 635 mm ID are used to convey corrosive fluids.

Towers, entrainment separators, thermowells, and rupture disks are fabricated of impervious graphite material. Many equipment items are available from stock. Special equipment can be custom-designed and built, and both standard and special items can be integrated to handle a complete process step. Systems for the absorption of hydrogen chloride in water to produce hydrochloric acid use impervious graphite equipment throughout. Usually, absorption is done in a falling-film absorber (84), a special design adaption of the shell and tube heat exchanger. This approach to absorption of hydrogen chloride (18) was developed and expanded in the United States and is now accepted as the standard.

Stripping hydrogen chloride (82–88) from aqueous hydrochloric acid and the subsequent production of anhydrous hydrogen chloride can be efficiently and economically achieved with a series of impervious graphite shell and tube heat exchangers that operate as falling-film reboiler, water and brine-cooled condensers, and bottoms acid cooler. In plants with available chlorine and hydrogen, the production of hydrogen chloride in any form or concentration can be achieved in a system that combines the burning of hydrogen in chlorine in a water-cooled graphite combustion chamber; absorption is carried out in an impervious graphite falling-film absorber, and a train of impervious graphite exchangers is used for stripping and drying (89).

Low Permeability Graphite. Most resin-impregnated impervious graphite materials have a maximum operating temperature limit of 170°C because of resin breakdown above this temperature. Certain special grades with a temperature limitation of 200°C are on the market (90). The chemical industry has developed high temperature processes (370°C and above) where equipment corrosion is a serious problem. Graphite equipment could solve the corrosion problem, but complete fluid containment is usually needed. To meet this need, graphite manufacturers have developed low permeability graphite materials where permeability is reduced by deposition of carbon and graphite in the pores of the base material (90). This material is not limited in its operating temperature, except in oxidizing conditions, and it is used to fabricate high temperature interchanger ejectors, fused salt cells, fused salt piping systems, and electric resistance heaters.

Porous Graphite. Several grades of low density, porous carbon and graphite are commercially available. A controlled combination of high permeability and porosity characterizes these materials. Average pore diameters for typical grades are 0.03–0.12 mm with a total porosity of 48%. Porous graphite is manufactured by graphitizing the amorphous material.

Porous carbon and graphite are used in filtration of hydrogen fluoride streams, caustic solutions, and molten sodium cyanide; in diffusion of chlorine into molten aluminum to produce aluminum chloride; and in aeration of waste sulfite liquors from pulp and paper manufacture and sewage streams.

5.3. Mechanical Applications. Carbon-graphite possesses lubricity, strength, dimensional stability, thermal stability, and ease of machining, a combination of properties that has led to its use in a wide variety of mechanical applications for supporting rotating or sliding loads in contact. Its principal applications are in bearings, seals, and vanes, which are in sliding contact with a partner material. Mechanical applications of carbon-graphite include face, ring, and circumferential seals for gases and fluids both corrosive and noncorrosive; carbon cages for roller and ball bearings, carbon sleeve bearings and bushings, carbon thrust bearings or washers, and combination sleeve/thrust bearings; packing rings for steam and water valve shafts and packing rings for compressor tail rods; and nonlubricated compressor parts such as piston rings, wear rings, segments, scuffer shoes, shaft tail-rod packing rings, pistons, and piston skirts. Miscellaneous applications include flat-plate slider parts for supporting machinery and facilitating sliding movement under load; and rotor vanes and metering device parts.

Carbon-graphite materials employed for mechanical applications are prepared by mixing selected sizes and types of carbon and graphite with binder materials such as pitches and resins. The mixtures are formed into compacts and baked to temperatures of ca 1000–3000°C. Specific raw materials and processing techniques are employed to obtain desired properties for the finished carbon-graphite materials (91).

The successful application of carbon-graphite as a sliding contact depends on the proper use of additives and impregnants in the carbon-graphite materials. Carbon-graphite, long considered to be self-lubricating, depends on the presence of adsorbed films of water vapor and/or oxygen for its low friction and low

wear properties. This adsorbed boundary layer is soon lost when the operation is conducted at high altitude, high temperature, or in cold, dry air. A substitute boundary layer can be formed by incorporating additives such as metallic sulfides, oxides, and halides, and impregnants such as thermoplastic and thermosetting resins. Additives and impregnants also serve to improve oxidation resistance, provide impermeability to high pressure gases and liquids, and even permit operation under high vacuum conditions (92), a primary requirement of equipment used for exploring outer space.

Carbon-graphite materials do not gall or weld even when rubbed under excessive load and speed. Early carbon materials contained metal fillers to provide strength and high thermal conductivity, but these desirable properties can now be obtained in true carbon-graphite materials that completely eliminate the galling tendency and other disadvantages of metals.

5.4. Electrode Applications. With the exception of carbon use in the manufacture of aluminum, the largest use of carbon and graphite is as electrodes in electric-arc furnaces. In general, the use of graphite electrodes is restricted to open-arc furnaces of the type used in steel production; whereas, carbon electrodes are employed in submerged-arc furnaces used in phosphorus, ferroalloy, and calcium carbide production.

Graphite Electrodes. Graphite electrodes are commercially produced in many sizes ranging from 32 mm diameter by 610 mm length to 700 mm diameter by 2800 mm length, each diameter generally being available in two or three lengths. Such electrodes are used in open-arc furnaces for the manufacture of steel (93), iron and steel castings, brass, bronze, copper and its alloys, nickel and its alloys, magnesium, lead, tin, fused cast refractories, fused refractory grain, mineral wool insulation (94), and the treatment of toxic wastes (95). By far the largest use of graphite electrodes is in the manufacture of steel and, as a consequence, the growth of graphite production has been closely related to the growth in electric furnace steel production. Figure 10 is a schematic of a typical three-phase alternating current open-arc furnace, and shows the position of the three graphite electrode columns in this type furnace. A small but growing number of arc furnaces now use direct current and a single-electrode column positioned in the center of the furnace. In either case, steel is produced by filling the cylindrical shell with ferrous scrap, direct reduced iron, or occasionally, molten pig iron, then melting and refining the metallic charge with the intense heat derived from the electric arc generated at the tips of the electrodes.

Prior to the mid-1940s, the arc furnace was used almost exclusively for the production of low tonnage, high quality steels such as stainless and alloy steels. Since then, its use has been extended to production of the more common high tonnage steel grades, including sheet steels (see STEEL).

Graphite electrodes are consumed in the melting process. For iron and steel production, the average consumption is ca 2–5 kg/t, depending on the quality of the charge material, the quality of the electrodes, and numerous factors related to the productivity and operation of the arc furnace (96). A combination of these factors has resulted in a reduction of about 40% in specific electrode consumption over the past 15 years. Electrode consumption can be classified into three broad categories: tip consumption, sidewall consumption, and breakage. Roughly half of the observed consumption occurs at the electrode tip where the intensely

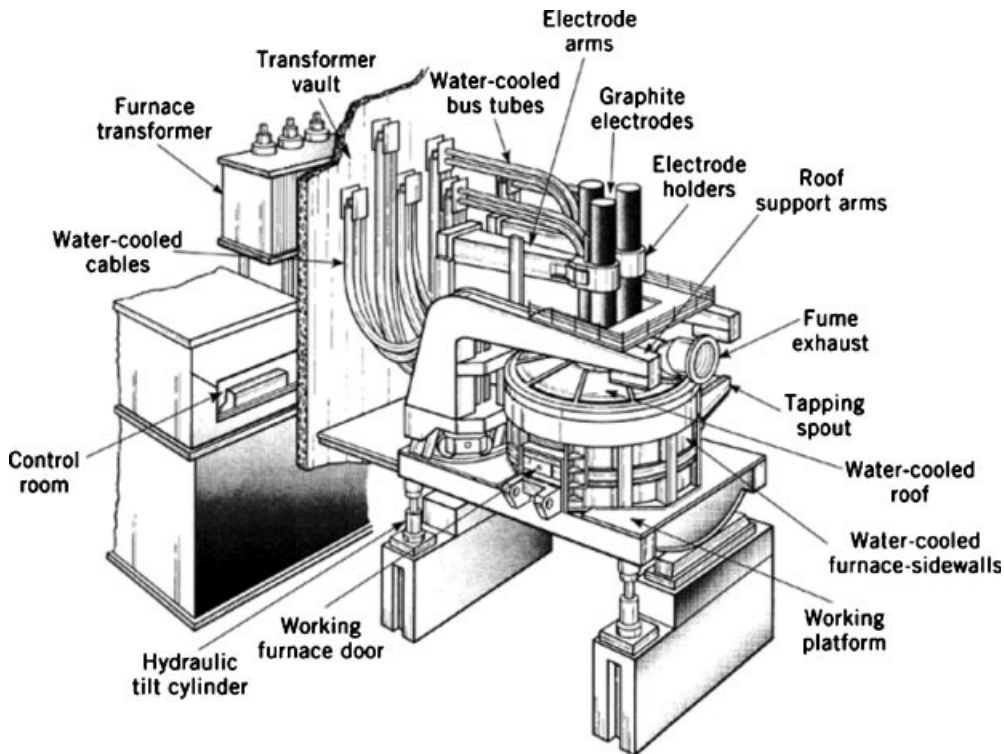


Fig. 10. Schematic of an electric-arc furnace. Courtesy of UCAR Carbon Technology Corp.

hot and rapidly moving arc spot produces both vaporization of the graphite and some ejection of small graphite particles. In addition, the electrode tip is eroded by contact with the liquid steel and slag. For a given electrode size, the rate of incremental tip consumption increases proportionally to the power and the square of the operating current (97). As a consequence, modern high power arc furnaces operate with high voltage, low current arcs in order to minimize electrode consumption. The periphery or sidewall of the hot electrode is slowly consumed by reaction with oxidizing atmospheres both inside and outside the furnace, resulting in tapering of the electrode toward the arc tip. Sidewall consumption is time dependent and is lowest for high productivity furnaces. Certain fume removal systems and the use of oxygen in the furnace for assisting melting and refining may increase sidewall consumption. Since sidewall consumption may account for 40% or more of total electrode consumption, extensive efforts have been made to reduce this component of consumption. Oxidation retardants, electrode coatings, and water-spray rings have been moderately successful in minimizing sidewall oxidation of the portion of the electrode outside the furnace. However, the extreme thermal and chemical environment inside the furnace has prevented to date similar reduction in sidewall consumption of electrodes once inside the furnace. A third form of consumption consists primarily of electrode breakage resulting from excessive movement of large masses of scrap during

melting or the presence of nonconductors in the charge. Although such breakage generally accounts for less than 5% of net electrode consumption, excessive thermal shock, improper joining practices, excessive electrode column vibration, incorrect phase rotation, and inappropriate power programs can magnify this form of electrode consumption (96). Although attempts have been made to correlate electrode consumption with relatively small changes in electrode properties, the significant reductions in electrode consumption achieved make it clear that charge quality, furnace productivity, and furnace operating practices exert a more profound influence on electrode performance. Most notable is the established inverse relationship between furnace productivity and electrode consumption.

As the electrode is consumed from the tip, the periodic addition of electrodes to the top of the columns becomes necessary. In most domestic steel plants, electrode additions are made on top of the furnace without removing the electrode columns. In certain countries, however, the electrode columns are removed from the furnace, and electrode additions are made in an assembly station adjacent to the furnace. A typical electrode column contains two full-length electrodes plus a portion of a third electrode that is partially consumed.

Two configurations are in common use for joining graphite electrodes. Both use tapered components with a thread pitch of either three or four threads per inch (2.54 cm). Electrodes of up to about 300 mm diameter frequently have one end machined with an external tapered male thread, whereas the other end contains an internally threaded female tapered socket. Two electrodes are joined by screwing the male end of one electrode into the female socket of the second electrode and applying the desired tightening torque. The more common system of joining electrodes is illustrated in Figure 11. In this case, an externally threaded,

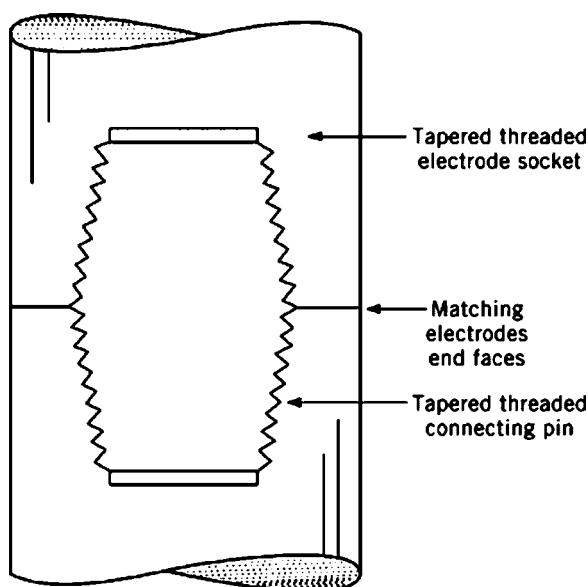


Fig. 11. Illustration of the use of a double-tapered connecting pin to join electrodes.

double-tapered connecting pin is used in conjunction with electrodes which have internally threaded tapered sockets in both ends. Prior to joint assembly, the connecting pin is screwed into the lower socket of the electrode to be added. This electrode is then raised, and the assembly screwed into the open socket of the other electrode on the furnace and torqued tight. Most electrode manufacturers now preset the connecting pin in one socket of each electrode prior to shipment in order to minimize potential electrode joining difficulties. National Electrical Manufacturers Association standards have been established for electrode sizes and for electrode socket and connecting pin configurations, sizes, and tolerances (98) in order to assure the interchangeability of electrodes and connecting pins from different manufacturers.

Graphite electrodes are produced in two broad-grade classifications, regular-grade and premium-grade. Typical room temperature properties of these grades are given in Table 8. The principal differences between the two grades are that the premium-grade is made from a superpremium needle coke and is pitch-impregnated prior to graphitization. The premium-grade electrode is used where very high performance is required, such as in the ultrahigh powered arc furnaces. The current-carrying capacity of an electrode column depends on many characteristics of the furnace operation as well as the characteristics of the electrode and electrode joint. Over the years, significant progress has been achieved in improving the current-carrying capacity of electrode columns.

Table 8. Typical Room Temperature Properties of Regular- and Premium-Grade Graphite Electrodes and Connecting Pins

Property ^a	Regular-grade electrodes	Premium-grade electrodes	Premium-grade connecting pins
bulk density, g/cm ³	1.60	1.70	1.80
resistivity, $\mu\Omega \cdot \text{m}$	7.3	5.5	4.2
flexural strength, kPa ^b			
wg ^b	6,900	9,100	20,000
cg	5,800	7,000	12,500
elastic modulus, GPa ^b			
wg	5.3	7.6	17
cg	3.5	5.0	6.9
coefficient of thermal expansion (CTE), $10^{-6}/^{\circ}\text{C}$			
wg	0.60	0.40	0.30
cg	1.40	1.10	2.20
thermal conductivity, W/(m · K) ^c			
wg	134	168	180
cg	67	101	110
thermal shock parameter ^d			
wg	290×10^3	490×10^3	700×10^3
cg	80×10^3	130×10^3	90×10^3

^awg = with – grain; cg = cross – grain.

^bTo convert Pa to psi, multiply by 1.45×10^{-4} .

^cMeasured.

^dThermal shock parameter = $\frac{\text{thermal conductivity} \times \text{strength}}{\text{CTE} \times \text{elastic modulus}}$

In service, graphite electrodes operate at up to 2500 K and are subject to large thermal and mechanical stresses and extreme thermal shock. Graphite is unique in its ability to function in this extreme environment. The relatively low electrical resistance along the length of the electrode minimizes the power loss owing to resistance heating and helps keep the electrode temperature as low as possible. This characteristic is most important in ultrahigh power furnaces where the approximately 30% lower electrode resistivity of premium-grade electrodes is usually essential for successful operation. A high value of the thermal shock parameter is also important (Table 8); this parameter is improved by high strength and high thermal conductivity combined with low elastic modulus and low coefficient of thermal expansion. The ability of graphite electrodes to withstand thermal shock has been increased significantly in the past decade as a consequence of enhancement in the elastic modulus and coefficient of thermal expansion resulting from improved raw materials and advanced manufacturing technology.

The joints between electrodes are an extremely important part of the electrode system, both from the standpoint of resisting the mechanical forces of scrap caves and of carrying high electrical current density without localized overheating. To assure high mechanical and electrical performance of joints, electrode manufacturers carefully control the axial and radial thermal expansion characteristics of both the electrodes and the connecting pins, as well as the machining tolerances, in order to achieve the desired level of thermal tightening of the joint as the electrode column is heated in service. Such joints should possess high strength, especially in flexure, and possess very low electrical contact resistance. Careful assembly and proper torque are vital to good performance of electrode joints (96).

Carbon Electrodes. Carbon electrodes are rigid carbonaceous shapes deployed in electric furnaces. They are the final link in the chain of conductors from the energy source to the reaction zone of an electrically heated vessel. The gap bridged by the electrode is that between the contact plates that transmit current to the electrode and the discharge area at the arc end of the electrode.

Two types of carbon electrodes are in widespread use. Prebaked carbon electrodes (Fig. 12) are those made from a mixture of carbonaceous particles and a coal-tar pitch binder. The electrode is formed by extrusion or molding from a heated plasticlike mix and subsequently baked. Final bake temperature is sufficient to carbonize the binder, ie, about 850°C. At this temperature the binder is set, all volatiles have left, and a significant portion of the product shrinkage has occurred.

Self-baked carbon electrodes are those whose shapes are formed *in situ* (99). The carbonaceous mixture is placed into a hollow tube-shaped metal casing. The upper end receives the unbaked mixture as a solid block, small particles, or warm plastic paste. The casing contains inwardly-projecting longitudinal perforated fins that become surrounded by baked carbon as the casing is incrementally moved downward and through the contact plates. Casing and carbon are consumed in this furnace.

Several systems are under development that will reduce or negate casing movement with the carbon (100–102). These will be more acceptable to furnace processes where product contamination by the casing material is undesirable.



Fig. 12. Prebaked electrodes. Courtesy of UCAR Carbon Technology Corp.

Two types of furnaces use carbon electrodes. In the open-arc the raw materials fed into the furnace do not contact the electrode. An arc is maintained between the electrode and the charged material or the liquid bath that results from melting the charge. A furnace producing molten steel from a charge of solid metallic scrap is an example of an open-arc. The development of graphite electrodes has practically eliminated carbon electrodes from most open-arc units. The graphite can conduct much more current per unit of cross-sectional area and use of carbon in modern high powered open-arc systems is not a practical choice. Carbon is still the electrode of choice for certain open-arc furnaces such as those that produce refractories and those utilized in slag cleaning facilities.

Submerged-arc furnaces are the other type of equipment using carbon electrodes. In these, the charge materials are in contact with the electrodes. Some of the energy imparted from the electrode may be in the form of an arc to the charge or to the bath. It also may flow between electrodes through a conductive charge. Submerged-arc furnaces are quiet because the sound generated by the arc is attenuated by the covering burden of charge material.

A variety of products are made in submerged-arc furnaces. Among them are various alloys and compounds. Each uses a particular type or grade of carbon electrode to hold production costs at the lowest possible level. Graphite electrodes could be and are used in some submerged-arc furnaces. Such a choice is the result of special conditions that warrant use of the more expensive graphite in lieu of carbon.

Ferroalloy and carbide producers are the largest volume users of carbon electrodes. These are the self-baking type and ferrosilicon is the dominant product. Prebaked cathodes are used to produce silicon where a low iron content in the metal is required. A typical open top submerged-arc furnace is shown in Figure 13. Two silicon grades dominate the market; chemical-grade for producing silicones, and metallurgical-grade for alloying with aluminum. Another important use of prebakes is in the production of thermal phosphorus to be

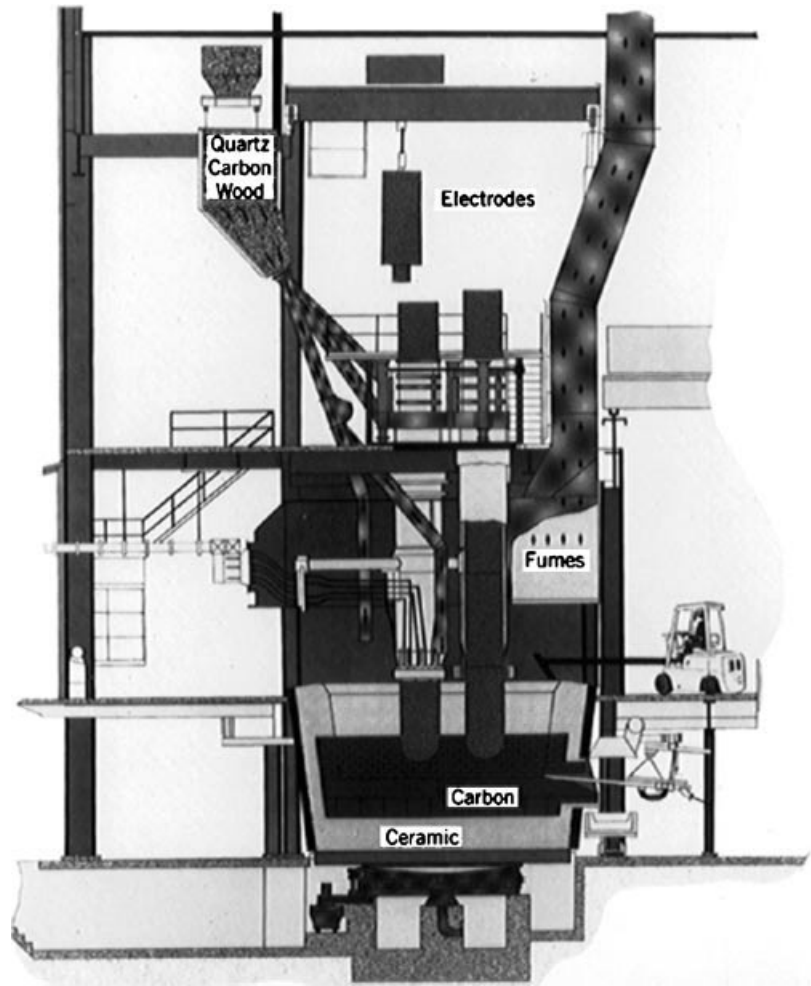


Fig. 13. Typical silicon metal furnace. Courtesy of UCAR Carbon Technology Corp.

used for the manufacture of high purity phosphoric acid. These furnaces are sealed. A typical phosphorus furnace is shown in Figure 14.

Several grades of carbon electrodes are available. The characteristics of each result from the raw materials and processes used in manufacturing. The generic descriptions and primary constituents are as follows:

Coal electrodes	The primary constituent is calcined anthracite coal particles.
Coke electrodes	The primary constituent is calcined petroleum coke particles.
Semigraphite electrodes	The primary constituent is sized graphite particles.
High purity electrodes	The final product has a low ash and/or low iron content achieved by raw material selection or special processing.

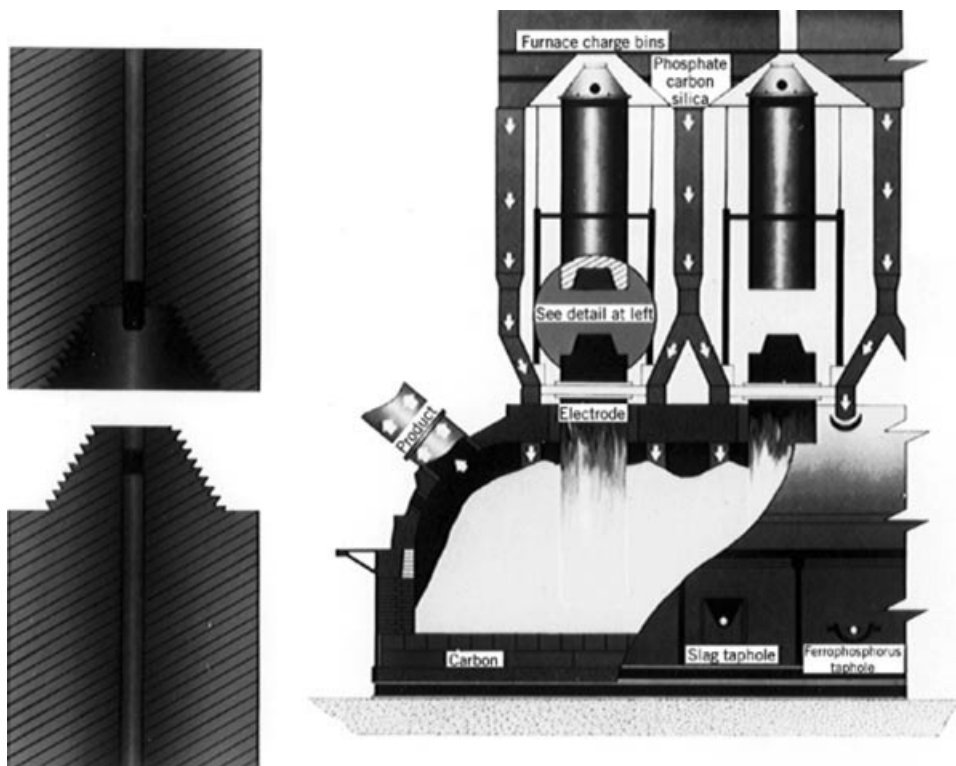


Fig. 14. Typical phosphorus furnace. Courtesy of UCAR Carbon Technology Corp.

All carbon electrodes are amorphous. They are formed from a mixture of particles, fillers, and a binder, and they are baked to about 850°C. This is not high enough to cause the development of a crystalline structure as would occur if the temperature was elevated to that needed for graphitization.

Prebaked carbon electrodes are manufactured in all diameters up through 1500 mm. Some prebakes are produced as quadriforms to suit specific furnaces. Self-baking electrodes are in service through 2134 mm diameter. Electrode lengths are as needed for particular applications. Rounds are available in lengths up to 2794 mm and quadriforms as long as 3556 mm. Self-baked electrodes are continuous.

Production of carbon electrodes is a capital-intensive business. Two suppliers dominate the prebaked market. Carbon paste producers are more numerous and tend to serve local markets. There is no international standard for the threaded joints on carbon electrodes. Manufacturers of straight pin carbon electrodes have followed the physical specifications adopted for graphite electrodes (103). Unified standards do not exist for pinless joints resulting in limited interchangeability among brands. Electrode diameters are offered in both English and metric sizes with no restrictions on new or unique diameters.

The physical properties of carbon electrodes are determined by the raw materials and processes used in their manufacturer. There are no universal

Table 9. Ranges of Physical Properties of Typical Carbon Electrode Grades

Property	Range
apparent density, g/mL	1.50–1.68
specific resistance, $\mu\Omega\cdot\text{m}$	21–50
flexural strength, MPa ^a	3.1–6.9
Young's modulus, GPa	4.1–8.8
ash content, wt %	0.6–8.0

^aTo convert MPa to psi, multiply by 145.

grade designations and the published properties are quite broad. Table 9 shows ranges for some of the common commercially available grades.

The density, flexural strength, and electrical conductivity increase with greater amounts of graphite particles in the mix. Flexural strength and Young's modulus move together. Ash increases in proportion to the amount of coal in the mix. Higher graphite content increases the electrode cost. Users select that electrode which gives the lowest bottom line cost per unit of production. The stated properties cannot be equated to performance. The user needs to resolve the overall performance in actual production to determine the best grade for the specific application.

All electrodes pass through the contact pads of the electrode holder and terminate some distance above the furnace hearth. As it is consumed, the electrode is slipped downward. Self-baked electrodes are continuous and the slipping rate can be only as rapid as baking allows. Prebaked rounds are connected axially one to another with threaded features (Fig. 15). A carbonaceous connecting

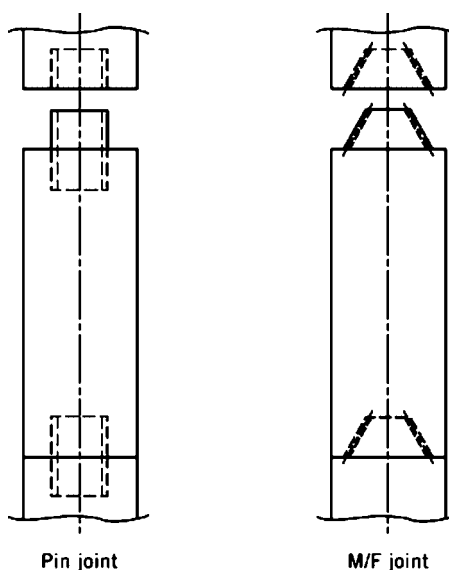


Fig. 15. Prebaked electrode joints. Courtesy of UCAR Carbon Technology Corp.

pin, usually made of graphite, is threaded into sockets in the ends of two axially aligned electrodes. Forming a male (external) thread on one electrode permits its connection into a threaded female (internal) socket on the other electrode. Quadriform electrodes are firmly connected to the source of power and are suspended, keeping the electrode vertical in the furnace. When the usable length of the quadriform is consumed, the remainder of the electrode is removed and replaced with full-length stock. One form of the noncircular electrode is called a packet. A few packet furnaces are still in operation.

There is no limit to the possible configurations of electric furnaces. They exist as single-phase or polyphase, a-c or d-c, and one to six or more electrodes. The furnace cross sections can be round, heart-shaped, oval, rectangular, or variations of each. Some furnaces, especially those for silicon production, have a rotating hearth and shell.

Carbon electrodes are the normal choice for the link in the connection chain to deliver power to the arc tip. Graphite may be used in special applications, but the higher cost of graphite favors the use of carbon electrodes. Carbon possesses properties ideal to its application as an electrode. These properties include no softening point, no melting point, electrical conductivity, strength increases with increasing temperature, resistivity drops as temperature increases, available in the size and purity desired, and cost effectiveness.

Pin-type electrode connections are engineered to perform across a wide temperature range. Thermal tightening is a feature that causes increasing unit contact pressure on the end faces and the contacting thread flanks. Axial CTE of the carbon is greater than the axial CTE of the pin. Transverse CTEs are controlled to either add to or not detract from the axial tightening effect. The magnitude of the thermal tightening is often such that permanent tensile elongation occurs in the pin and permanent compressive deformation occurs at the end faces. As a result, the joint will open when it is cooled sufficiently, because the elastic limits of the pin and electrodes had been exceeded.

The mechanisms of electrode consumption are dictated by the environment in which the electrode operates. Oxidation occurs on those surfaces exposed to oxygen when they are above the oxidation threshold temperature. Erosion removes carbon as it is abraded through its contact with the charge material or from movement of the electrode in the burden. The electrode is constantly repositioned in the axial direction as necessary to maintain a desired arc length. Part of the tip losses result from sublimation. At the tip there is particle loss resulting from the detonation effect of an alternating current arc. A portion of the electrode enters the electro-thermal reduction process. The electrode becomes a reductant if the charge mixture is carbon "short," ie, less than stoichiometric. The loss of large or massive amounts follows column breakup from cracks and splits in the structure or from a full break across the electrode cross section.

Self-baking carbon electrode columns have longitudinal fissures. This results from melting or oxidation of the casing fins that extend inwardly from the casing. These fissures act as crack stoppers, but they also generate additional exposed area for oxidation. Joints in prebaked electrode columns that do not remain tight become open at the end faces. Socket splitting and cross cracks usually occur. If these joints survive to the arc region, the splits and cracks can propagate and cause chunking of the carbon. These rather large pieces are

undesirable for several reasons. They can upset the reaction in progress at the arc tip, they are a cause of inefficient electrode utilization, and they may foul tap holes thereby impeding proper furnace operation.

The demand for self-baking carbon electrodes is keyed to the steel industry since it is the principal consumer of ferroalloys. Demand for prebaked electrodes is predicted to grow through the year 2000 at an annual rate of about 5%. The demand for chemical-grade silicon is the driving force for this growth. Production of metallurgical-grade has a positive but lower growth rate than that for chemical-grade silicon. Usage in production of elemental thermal phosphorus is predicted to be stable since improvements in the wet acid process can supply the increasing demand for high purity phosphoric acid.

Although carbon electrode production has been regarded as a mature business, the steady growth in demand and the need for improved electrodes has prompted ongoing development efforts in these areas: (1) cost containment through raw material substitutions and process improvements; (2) higher purity electrodes for those processes such as silicon production; (3) improvements in thermal shock resistance to enhance electrode performance; and (4) better joining systems for prebakes.

Anode Applications. Graphite has been used as the primary material for electrolysis of brine (aqueous) and fused-salt electrolytes, both as anode and cathode. Technological advances, however, have resulted in a dimensionally stable anode (DSA) consisting of precious metal oxides deposited on a titanium substrate that has replaced graphite as the primary anode (104–107) (see ALKALI AND CHLORINE PRODUCTS).

The cell is the basis of all electrolysis. The anode admits current into the electrolyte and the cathode serves as a means of exit for the electrical current. The electrical flow provides a definition for electrolysis: the flow of current from the anode through the electrolyte and out of the cell through the cathode with ensuing decomposition of the electrolyte, with products being formed at the electrodes.

Graphite properties conducive to successful electrolytic application include high electrical conductivity, high degree of insolubility and operation at low voltage, high purity, low initial cost, easily machinable, and few limitations as to size and shape.

The service life of graphite anodes largely depends on three factors: (1) electrochemical attack by nascent oxygen, resulting from oxidation at the surface; (2) chemical attack through the chemical reaction of cell products; and (3) mechanical loss of material as a result of (1) and (2). Although the eventual service life is limited by these three factors, it is not uncommon for graphite anodes to provide 300–700 days of service life. Anode operating life is also influenced by a number of cell operating variables, such as cell temperature, brine flow rate, brine concentration, and the current density imposed on the anode.

The two basic types of graphite anodes used are plain and impregnated. Impregnation prevents anolyte penetration of the graphite pores and resultant corrosion from within. For impregnated anodes, base graphites with initial porosities of 15 to 30% are given a vacuum-pressure impregnation usually with an oil, such as linseed, to fill or coat the accessible pores. For some low temperature electrolysis applications, resin treatments such as phenolics are used. These

applications are well below the temperature limitations of these resins. Proper impregnation provides a 25 to 50% increase in anode life over unimpregnated graphite.

Chemical Production. Electrolytic production of chemicals is conducted either by solution (water) electrolysis or fused-salt electrolysis. Fluorine, chlorine, chlorate, and manganese dioxide are liberated from water solutions; magnesium and sodium are generated from molten salt solutions.

Fluorine. This application uses carbon plates as the anode in a fluorine salt solution. Since the ordered crystal structure of graphite results in short life, carbon is the preferred anode material (see FLUORINE).

Chlorine. Most processors have converted from graphite to metal anodes. The two basic designs were diaphragm cells, which used graphite plates as anodes, and mercury cells in which a layer of mercury acted as the cathode with intricately machined graphite blocks as the anode (108).

Chlorate. Conversion to metal anodes has also taken place in this process. Sodium hydroxide, which is formed at the cathode, reacts to form the sodium chlorate product (see ALKALI AND CHLORINE PRODUCTS).

Manganese Dioxide. Graphite plates used as anodes in this process are coated with MnO_2 during electrolysis. The anodes are removed from the solution periodically and the MnO_2 is removed by mechanical methods. Graphite can also be used as the cathode material. Titanium is used as anode materials where high quality MnO_2 is desired.

Magnesium. This molten salt electrolysis process is the current principal method of magnesium production. The graphite anodes can be either round or rectangular in nature (see MAGNESIUM AND MAGNESIUM ALLOYS).

Sodium. In this process, sodium is produced from molten salt. Individual cells are made up of a number of large round anodes (25–50 cm diameter) and steel pipe cathodes (see SODIUM AND SODIUM ALLOYS).

Cathodic Protection. Another application for graphite anodes is for cathodic protection. All metal structures placed on or underground are subject to corrosion by galvanic action. Current flow, either localized or general, results in oxidation, ie, rusting, of steel. Graphite anodes are used for impressed current protection and a current is induced in the circuit counter to the galvanic current. Since the polarity is reversed, the steel does not corrode. The graphite is normally impregnated with linseed oil resin impregnates to enhance life and an electrical connection is made inside the anode with a copper wire that is ultimately connected to steel to be protected. Life of the anode can range from 3–30 years in cathodic protection applications (109,110).

The low cost, light weight, and excellent electrical conductivity of graphite anodes have made this impressed current protection system valuable for cathodic protection of pipelines, storage vessels, process equipment, and also for well casings both on- and offshore.

5.5. Metallurgical Applications. Because of their unique combination of physical and chemical properties, manufactured carbons and graphites are widely used in several forms in high temperature processing of metals, ceramics, glass, and fused quartz. A variety of commercial grades is available with properties tailored to best meet the needs of particular applications (111). Industrial carbons and graphites are available in a broad range of shapes and sizes.

Structural Graphite Shapes. In many metallurgical and other high temperature applications, manufactured graphite is used because it neither melts nor fuses to many common metals or ceramics, exhibits increasing strength with temperature, has high thermal shock resistance, is nonwarping, has low expansion, and possesses high thermal conductivity. However, because of its tendency to oxidize at temperatures above 750 K, prolonged exposure at higher temperatures frequently necessitates use of a nonoxidizing atmosphere. In addition, prolonged contact both with liquid steel and with liquid metals that rapidly form carbides should be avoided.

Some of the more common applications for structural graphite shapes are (1) hot-pressing molds and dies (112) for beryllium at 1370 K and 6.9 MPa (1000 psi); diamond-impregnated drill bits and sawtooth segments at 1250 K and 13.8 MPa (2000 psi); tungsten and other refractory metals and alloys up to 2370 K and 6.9 MPa (1000 psi); and boron nitride and boron carbide up to 2060 K; (2) molds for metal casting steel railroad car wheels made by the controlled-pressure pouring process (113); steel slabs and billets made by the controlled-pressure pouring process (114); continuous casting of copper and its alloys, aluminum and its alloys, bearing materials; zinc and its alloys; and gray iron (115,116); centrifugal casting of brasses, bronzes, steels, and refractory metals (117); nickel anodes; welding rods and thermite welding molds; shapes of refractory metals (Ti, Zr, Mo, Nb, and W) and carbides; and shapes of gray, ductile and malleable irons (118); (3) foundry accessories including: mold chill plates, core rods, and riser rods; crucible skimmer floats; plunging bells for magnesium additions to ductile iron and desulfurization of blast-furnace hot metal (119,120); stirring rods for nonferrous metals; and railroad brake shoe inserts; (4) injection tubes and nozzles for purifying molten aluminum (121) and other nonferrous metals, desulfurization of blast furnace and foundry iron with calcium carbide or magnesium, and carbon raising of foundry iron with graphite powders; (5) aluminum extrusion components including dies, guides from die openings, run-out table boards, and cooling-rack inserts; (6) rolls for handling metal sheets are used in certain processes because they are self-lubricating and reduce surface marring; (7) immersion thermocouple protection tubes for nonferrous metals; (8) welding electrodes for welding, gouging, and cutting iron and steel, particularly with the aid of an air blast (122); (9) crucibles, either induction or resistance heated, for producing tungsten carbide, beryllium fluoride and beryllium, titanium and zirconium fluoride, semiconductor crystals germanium and silicon, and for laboratory chemical analysis equipment; (10) ceramic and glass production including: inserts for glass bottle takeout holders, casting molds for fused-cast refractories of alumina, magnesium, and chrome–magnesite composition up to 2650 K (127); mold susceptors for fabricating fused magnesia crucibles; susceptors, electrical resistor elements, fusion crucibles, molds and dies for the production of fused quartz (124); linings for float-glass plate production; and linings for hydrofluoric acid tanks for glass etching; (11) boats, trays, and plates for sintering clutch plates, brake disks, and cemented carbides and for the manufacture of semiconductor material and transistors; (12) furnace jigs for brazing honeycomb panels, automotive ignition points and arms, automotive radiator cores, transistor junction assemblies, and glass-to-metal seals; and (13) tooling for forming high temperature composite resin system aircraft parts (125).

Electric Heating Elements. Machined graphite shapes are widely used as susceptors and resistor elements to produce temperatures up to 3300 K in applications utilizing nonoxidizing atmospheres. The advantages of graphite in this type of application include its very low vapor pressure (lower than molybdenum), high black body emissivity, high thermal shock resistance, and increasing strength at elevated temperatures with no increase in brittleness. Graphites covering a broad range of electrical resistivity are available and can be easily machined into complex shapes at lower cost than refractory metal elements. Flexible graphite cloth is also used widely as a heating element since its low thermal mass permits rapid heating and cooling cycles. Typical applications include molten-iron or steel-holding furnaces, continuous casting tundishes, liquid-steel degassing units, chemical reaction chambers, quartz-fusion apparatus, zinc-vaporization chambers, sintering furnaces, vapor deposition units (qv) (126,127), and single-crystal silicon ingot growing furnaces (Czochralski method). In the furnaces that use vacuum or inert gas atmospheres, porous carbon or graphite, flexible carbon or graphite felts, and rigid fibrous graphite thermal insulation materials are extensively used.

Carbon and Graphite Powder and Particles. Manufactured graphite powders and particles are used extensively in metallurgical, chemical, and electrochemical applications where the uniformity of physical and chemical characteristics, high purity, and rapid solubility in certain molten metals are important factors (128). The many grades of carbon and graphite powders and particles are classified on the basis of fineness and purity. Graphite particles and a process for production has been described (129). Applications for these materials include facings for foundry molds and steel ingot molds; additives to molten iron to control carbon level and chill characteristics; covering material for molten nonferrous metals and salt baths to prevent oxidation; additives to sintered materials to control carbon level and frictional characteristics; additions in oil, grease-, and oil-less bearings; oil well drill bit lubricant; and as charge-carbon and slag foaming agents in steel made in electric arc furnaces. The electrical and thermal conducting characteristics of carbon and graphite powders and particles account for their use as additives in dry cell batteries (130), paint (131), thermoset polybutadiene composites (132), ground anode backfill, concrete and corrosion-resistant sulfur concrete.

5.6. Refractory Applications. Various forms of carbon, semigraphite, and graphite materials have found wide application in the metals industry, particularly in connection with the production of iron, aluminum, and ferroalloys. Carbon has been used as a refractory material since 1850, though full commercial acceptance and subsequent rapid increase in use has occurred only since 1945.

Carbon as a Blast Furnace Refractory. The first commercial use of carbon as a refractory for a blast furnace lining took place in France in 1872, followed in 1892 by a carbon block hearth in a blast furnace of the Maryland Steel Co. at Sparrows Point, Maryland. After a period of abated interest the excellent results obtained with several carbon hearths in England, Germany, and the United States during the late 1930s and early 1940s, renewed enthusiasm for the material. Although initially used only for the hearth bottom of blast furnaces, carbon, semigraphite, semigraphitized carbon, and graphite

refractories have been successfully applied to hearth walls, tuyere zones, boshes, and even the lower to midstack of modern, intensely cooled, high performance blast furnaces around the world (133). More than 400 individual carbon or graphite blast furnace linings have been installed in North America through mid-1990. Additionally, carbon has also been used extensively for iron trough, iron runner, and slag runner safety linings, especially when external cooling is employed to extend the life of the ceramic working linings.

Carbonaceous and graphitic materials possess important characteristics that make them ideal blast furnace refractories: (1) they do not soften or lose strength at high operating temperatures of approximately 1150–1200°C; (2) they resist attack by molten slag and iron; (3) their relatively high thermal conductivity, when combined with adequate cooling and proper design concepts, promotes the formation of solidified coatings of slag and iron on their hot face. These coatings prevent erosion from the molten materials and process gases, promoting long life (134); (4) they possess excellent resistance to thermal shock, preventing spalling and cracking which interrupts heat transfer to the cooling system and exposes more refractory surface area to chemical attack; (5) a positive, low coefficient of thermal expansion provides dimensional stability and tightening of joints in the multipiece linings. However, because of their relatively low threshold temperature for oxidation from steam, carbon dioxide, or air, care must be taken to limit their exposure to these elements and maintain proper cooling at all times, to minimize damage from these temperature-dependent reactions (135,136).

The prime requirement of any carbonaceous material used in the blast furnace hearth wall or bottom is to contain liquid iron and slag safely within the crucible, throughout extended periods of continuous operation, often up to 15 years.

This requirement is most readily achieved if the lining design concepts employed and the carbonaceous or graphitic materials utilized with these concepts, combine to provide a refractory mass free from cracking caused by mechanical and thermal stress (137). Additionally, the refractory materials must exhibit thermal conductivities that are high enough to permit the formation of solidifying layers of iron and slag on their hot faces and permeabilities that are low enough to prevent the impregnation of the refractories by alkalis and other process contaminants (138). It is also helpful if the refractory materials themselves are resistant to attack from alkalis by virtue of the inclusion of various additives during their manufacture (137). Proper cooling of the materials also contributes to their longevity.

For practical reasons, the blast furnace hearth is divided into two principal zones: the bottom and the sidewalls. Each of these zones exhibits unique problems and wear mechanisms. The largest refractory mass is contained within the hearth bottom. The outside diameters of these bottoms can exceed 16 or 17 m and their depth is dependent on whether underhearth cooling is utilized. When cooling is not employed, this refractory depth usually is determined by mathematical models; these predict a stabilization isotherm location which defines the limit of dissolution of the carbon by iron. Often, this depth exceeds 3 m of carbon. However, because the stabilization isotherm location is also a function of furnace diameter, often times thermal equilibrium cannot be achieved without some form of underhearth cooling.

This cooling can be accomplished by utilizing water, oil, induced or forced draft air, or passively, with a thick layer of high thermal conductivity graphite. The use of underhearth cooling not only allows a thermal equilibrium to be achieved but also permits a shallower depth of refractory to be used, reducing lining cost. The cooling system can employ a pipe system or airtight steel plenums (139).

The main mechanisms of hearth bottom wear are high heat load, chemical attack, erosion from molten liquids, mechanical and thermal stress, and penetration because of ferrostatic and process pressure. A variety of special purpose carbons have been developed to minimize or eliminate the damage caused by these wear mechanisms.

In North America the individual blocks of carbon used in the hearth bottom have exceeded 6 m in length. In Europe and Asia these blocks are much shorter because of manufacturing capabilities. The longer bottom blocks permit the spanning of the hearth diameter with only two pieces, which prevents flotation of the carbon by the denser molten iron. This is because the bearing provided by the dead load of the hearth walls, which rest on the ends of the carbon block "beams," anchors the bottom blocks and prevents flotation. If smaller blocks are utilized with two or more joints across the bottom, special reverse taper mating surfaces or interlocking techniques are required to prevent block flotation.

Occasionally the carbon bottom blocks in the lower most course are arranged vertically in "soldier block" fashion. The theory is that this arrangement permits the greatest heat-transfer capability of the material because of its anisotropy. Because these carbon blocks are usually extruded or pressed, there can be a 10% higher thermal conductivity in the direction perpendicular to the pressing direction and this practice takes advantage of this carbon characteristic. However, the vertical blocks in this configuration are more susceptible to differential temperature-induced stress and cracking. These designs are most prevalent in Russia and other Eastern European countries utilizing their technology.

The latest design philosophy is to utilize various types of ceramic refractories as the working lining on top of the carbon bottom. This relegates the carbon material in the bottom to a cooling function instead of a crucible function, since the molten liquids are contained completely within the ceramic layers. The high conductivity of the carbon or graphite used as the cooling layer permits thermal equilibrium to be achieved while the liquid iron is still within the ceramic. One European ironmaker has dispensed with all carbon in the hearth bottom and instead utilizes a graphite-cooled ceramic bottom, promoting this concept worldwide.

The hearth wall zone of the blast furnace presents different design problems and exhibits different main mechanisms of wear. Because these linings must contain molten iron, water cooling must be maintained on the external furnace jacket, either utilizing flooded water jackets or spray showers or by the use of water-cooled, cast-iron stave coolers located within the vessel at the cold face of the refractories. Heat removal, therefore, must travel through the wall thickness to the cooling element. Thus the design concepts employed as well as the properties of the refractory utilized have a direct bearing on the success of the hearth wall.

In North America, a special, high conductivity, low permeability, "hot-pressed" carbon brick is utilized almost exclusively for hearth walls. Because of their relatively small size and special, heat setting resin cement, and because the brick is installed tightly against the cooled jacket or stave, differential thermal expansion can be accommodated without refractory cracking and effective cooling can be maintained. Additionally, the wall thickness is generally smaller than 1 m, which promotes the easy formation of a protective skull of frozen materials on its hot face. Thus hearth wall problems and breakouts because of carbon wall refractory failure are virtually nonexistent.

Elsewhere, large block carbons are utilized as wall material, generally with thicknesses in the range of 1.5–2.5 m. However, the single-thickness blocks have a tendency to crack and spall because of high mechanical and thermal stress and lack of expansion provisions. To combat this problem, various exotic carbons have been developed to resist hot metal penetration and increase thermal conductivities, but it should be noted that these measures do not solve the cause of the cracking, which is a lack of provisions to accommodate differential expansion.

Another problem inherent to large block designs is the fact that ramming materials must be utilized to fill the annulus that forms between the circular shell or staves and the large cross-section carbon block. Usually this annulus is 75–150 mm thick. The ramming materials used to fill this annulus always possess thermal conductivities that are severely affected by shrinkage of the ram, improper rammed density, deterioration over time because of contamination from leaking cooling water or the process environment. As a result, this rammed gap acts as a thermal barrier to effective heat transfer to the cooling system. The result is a higher carbon wall temperature with consequent accelerated wall wear.

This wear is caused primarily from high thermal and mechanical stress, chemical attack, attack by iron and slag, oxidation, and severe thermal shock. Thus the design of the hearth wall and the concepts employed are just as important as the carbon or graphite materials chosen for the refractory material. Despite their benefits and properties, no carbon or graphite material can overcome the problems of an improper hearth wall design concept.

In the early 1960s, the use of carbon and more recently, semigraphite and graphite as bosh refractories, has found increased acceptance and resulted in longer furnace campaign life. As is the case in the hearth wall, long life is dependent on efficient cooling of the carbonaceous or graphitic material. Originally, all carbon materials were cooled on their cold face, either by external shell spray cooling or external water jackets. Later, cast-iron, water-cooled staves were successfully used to cool the cold face of the bosh wall. However, all of these cooling systems required that the heat travel completely through the wall to reach the cooling element. These cooling methods were employed as a result of the high risk of water leaks because of poor quality coolers. These leaks could prove disastrous because the leaking water and consequential steam would badly oxidize the surrounding carbon. However, dramatic improvements in copper cooling plate technology and casting practice and sophisticated water leak detection systems have combined to provide low risk, high efficiency, inserted copper cooler systems for carbonaceous or graphitic linings. This results

in lower refractory temperatures and, thus, lower chemical attack from alkalis, which are temperature-dependent reactions with carbon (140).

These advances in cooling technology have also provided an opportunity to extend the thermal shock and chemical resistance of graphitic materials above the bosh, into the blast furnace stack. It has been recognized by many blast furnace operators around the world that the most destructive wear mechanism in the upper bosh and lower to midstack level is thermal shock. It is also universally recognized that the only refractory material that can withstand the magnitude of the temperature peaks normally occurring in these blast furnace zones are graphitic in nature. Therefore, the combination of densely spaced, modern copper coolers with high quality semigraphite or graphite refractories has proven to be a successful extender of blast furnace campaign life (141). Several furnaces have recently been relined utilizing these concepts in Holland, Canada, Italy, and the United States; several others are planned in England and Central America. As a result, the percentage of carbonaceous and graphitic materials utilized in the blast furnace is increasing tremendously and this trend should continue into the late 1990s.

Refractories for Cupolas. In many ways, the use of carbon cupola linings has paralleled the application of carbon in the blast furnace. Carbon brick and block are used to line the cupola well (142) or crucible. When properly installed and cooled carbon linings last for many months or even years of intermittent operation. Their resistance to molten iron and both acid and basic slags provides not only insurance against breakouts but also operational flexibility to produce different iron grades without the necessity of changing refractories. Carbon is also widely used for the tap hole blocks, breast blocks, slagging troughs, and dams.

Refractories for Electric Reduction Furnaces. Carbon hearth linings are used in submerged-arc, electric-reduction furnaces producing phosphorus, calcium carbide, all grades of ferrosilicon, high carbon ferrochromium, ferrovandium, and ferromolybdenum. Carbon is also used in the production of beryllium oxide and beryllium copper where temperatures up to 2273 K are required.

The principles pertaining to carbon blast furnace hearths apply as well to submerged-arc furnace hearths. In some processes, such as in d-c arc furnaces, the electrical conductance of carbon is a most important factor. The long life of carbon linings in these applications is attributable to carbon's exceptional resistance to corrosive slags and metals at very high temperatures.

Refractories in the Aluminum Industry. Carbon materials are used in the Hall-Heroult primary aluminum cell as anodes, cathodes, and sidewalls because of the need to withstand the corrosive action of the molten fluorides used in the process (see ALUMINUM AND ALUMINUM ALLOYS). Production of one metric ton of molten aluminum requires about 500 kg of anode carbon and 7.5–10 kg of cathode blocks which is the largest industry usage of carbon materials. Aluminum smelters generally have an on-site carbon plant for anode production. Anode technology is focused on raw materials (petroleum coke and coal-tar pitch), processing techniques, and rodding practices (143).

Prebaked cathode blocks used today are electrically calcined anthracite coal, semigraphite, semigraphitized, or graphite composition (144). Desired cathode operating characteristics include resistance to sodium attack, high operating strength, low porosity, high thermal shock resistance, and low electrical

resistance. The use of graphitic prebaked cathode blocks is a balance among performance, power, life, and economics within the cell; coal-based carbon is still the predominant cathode block composition. Cathode technology developments include coatings of titanium diboride (145) for voltage reduction and cemented collector bar assembly practices (146).

Sidewall blocks are monolithic rammed carbon or prebaked carbon and graphite blocks. Thermal conductivity to maintain a ledge against the molten metal is the most significant sidewall operating parameter. Some pots utilize both carbon and graphite sidewall blocks to maximize performance in specific sidewall areas. Thermal shock resistance and strength are also desired sidewall properties. Low temperature resin cast carbon, ie, cold-cast materials, can also be used for corner block locations. Carbonaceous cements and pastes are used for joint integrity and thermal balance.

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