Kirk-Othmer Encyclopedia of Chemical Technology.

GRAPHITE, PROPERTIES OF ARTIFICIAL

1. 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 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.

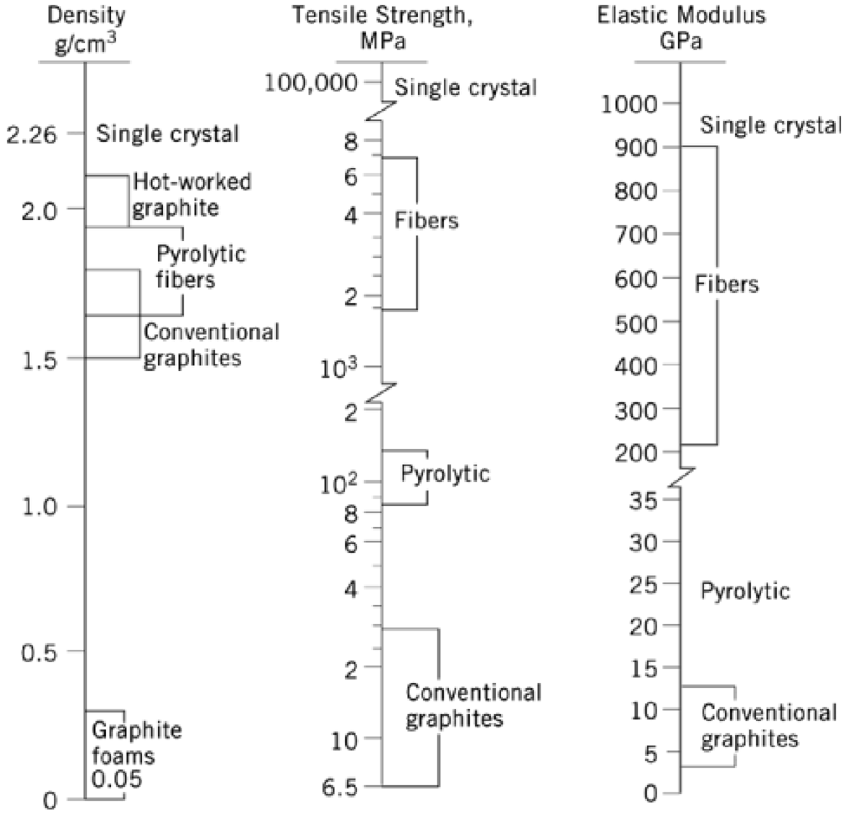

Fig. 1. With-grain mechanical properties of artificial graphite (1). To convert MPa to psi, multiply by 145.

2. 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 $0.40\mu\Omega\cdot\mathrm{m}$; 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 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 $\mu\Omega\cdot\mathrm{m}$, depending on the type of raw materials used. Graphites made from petroleum coke usually have a room temperature resistivity range of $5 - 15\mu\Omega\cdot\mathrm{m}$ 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.

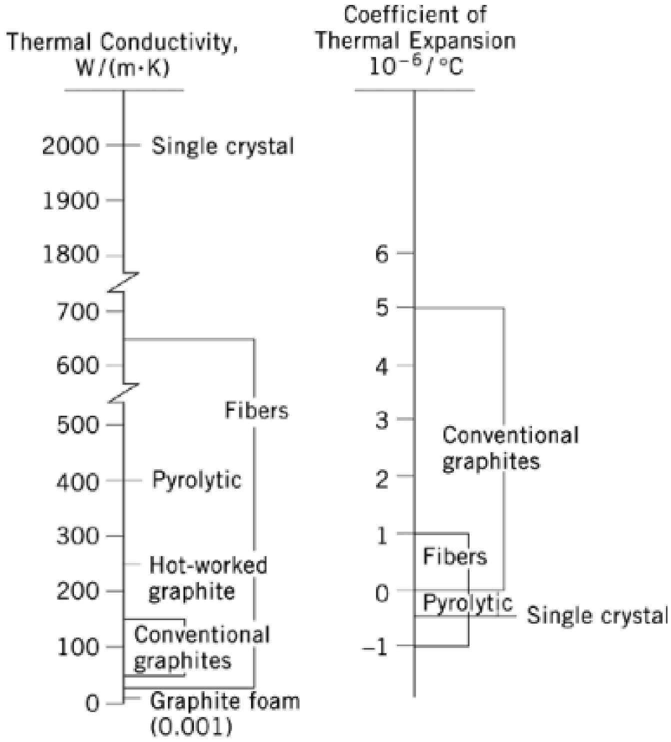

Fig. 2. With-grain thermal properties of artificial graphite (1).

Table 1. Properties of Graphite Crystals at Room Temperature[a]

Property	Value in basal plane	Value across basal plane
resistivity, $\mu\Omega$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, $^{\circ}C^{-1}$	-0.5×10^{-6}	27×10^{-6}

[a] Ref. 1.

[b] To convert GPa to psi, multiply by 145,000.

3. 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·K) and the electrical conductivity is in S(= 1/Ω) (12, 13). For most graphites, a value of thermal conductivity at room temperature accurate to ±5% can be obtained from the measured value of the electrical conductivity.

3.1. 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.

$$VTE = CTE_{\mathrm{wg}} + 2\,CTE_{\mathrm{cg}} \qquad (1)$$

At room temperature, the volume coefficient of thermal expansion of a single crystal is approximately $25 \times 10^{-6}/^{\circ}\mathrm{C}$ (14, 15), whereas those of many manufactured graphites fall in the range of $4 - 8 \times 10^{-6}/^{\circ}\mathrm{C}$. 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°C to the appropriate factor which varies from 0 at 100°C to 2.52×10^{-6} at 2500°C (19). This method is valid for stock of any grain orientation.

3.2. 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 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

Table 2. Elastic Constants of Graphite[a]

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

[a] Units c_{ij} (stiffness constant) in TPa, s_{ij} (compliance constant) in $(\mathrm{GPa})^{-1}$. To convert TPa to psi, multiply by 145,000,000.

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).

3.3. 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 temperature 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

Table 3. Properties of Fine- and Coarse-Grain Graphites[a, b, d]

Temp., °C	Thermal conductivity, W/(m·K)		*CTE*[b], cm/cm × 10^6/°C		Specific heat[c], kJ/(kg·K)	Tensile[d]				Compression[d]			
						Modulus, GPa		Strength, MPa		Modulus, GPa		Strength, MPa	
	wg	ag	wg	ag		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				

[a] wg = with – grain; ag = across – grain.

[b] CTE = coefficient of thermal expansion.

[c] To convert kJ to kcal, divide by 4.184.

[d] To convert MPa to psi, multiply by 145.

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).

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Carbon, structure, terminology and history; Graphite, artificial; Carbon, Structure, Terminology, and History; Graphite, Artificial; Graphite, Processing Artificial; Graphite, Applications of Artificial; Graphite, Specialty