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Review
Science and technology of graphite manufacture

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This review summarizes current descriptions of the science and technology of graphite manufacture. The delayed coking process is outlined and mechanisms of coke formation put forward including considerations of the composition of feedstocks. As graphite manufacture uses calcined delayed cokes of which the most valuable is needle-coke, a comparison of rotary kiln, rotary hearth and vertical shaft calciners is made. Grinding and sizing of calcined coke is important as this with the binder pitch leads to baked carbon. The stages in the manufacturing process are described as mixing, forming, extrusion, moulding, baking, impregnation and graphitization. The more advanced processing technology includes isostatic hot pressing, artifact densifications, high pressure impregnation/baking and binderless graphitization. A comprehensive list of references is included.

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1. Introduction

Synthetic graphites vary greatly in their density, electrical resistivity, mechanical strength, porosity and optical texture. This is because graphites have numerous uses and the detail of their specification controls their mode of manufacture and the source materials used for manufacture. Most synthetic graphites contain, among other components, a petroleum coke filler and a coal tar pitch binder which are mixed and then shaped by moulding or extrusion prior to graphitization. It is difficult to define the composition of graphite completely as the details of manufacture are often of a proprietary nature.

Detailed accounts of conventional processes employed in the manufacture of graphite have been published [1–3]. In general the process of the thermal conversion of organic materials to graphite can be considered as a dehydrogenative polymerization where hydrocarbon molecules lose hydrogen and combine to form larger planar networks [4, 5]. In industrial manufacture, this process is slow, taking up to 4 months [2] from the preparation of the raw materials to the despatch of the finished graphite.

Fig. 1 shows a model flow sheet for the manufacture of graphite. With the addition of a final machining stage, the essential steps in the manufacturing are [3]:

Preparation of raw materials
Mixing
Forming into green shapes
Baking
Impregnation
Re-bake option
Graphitizing
Machining ("Finishing" is the commercial term).

2. The delayed coking process

The principal raw material used as the filler phase

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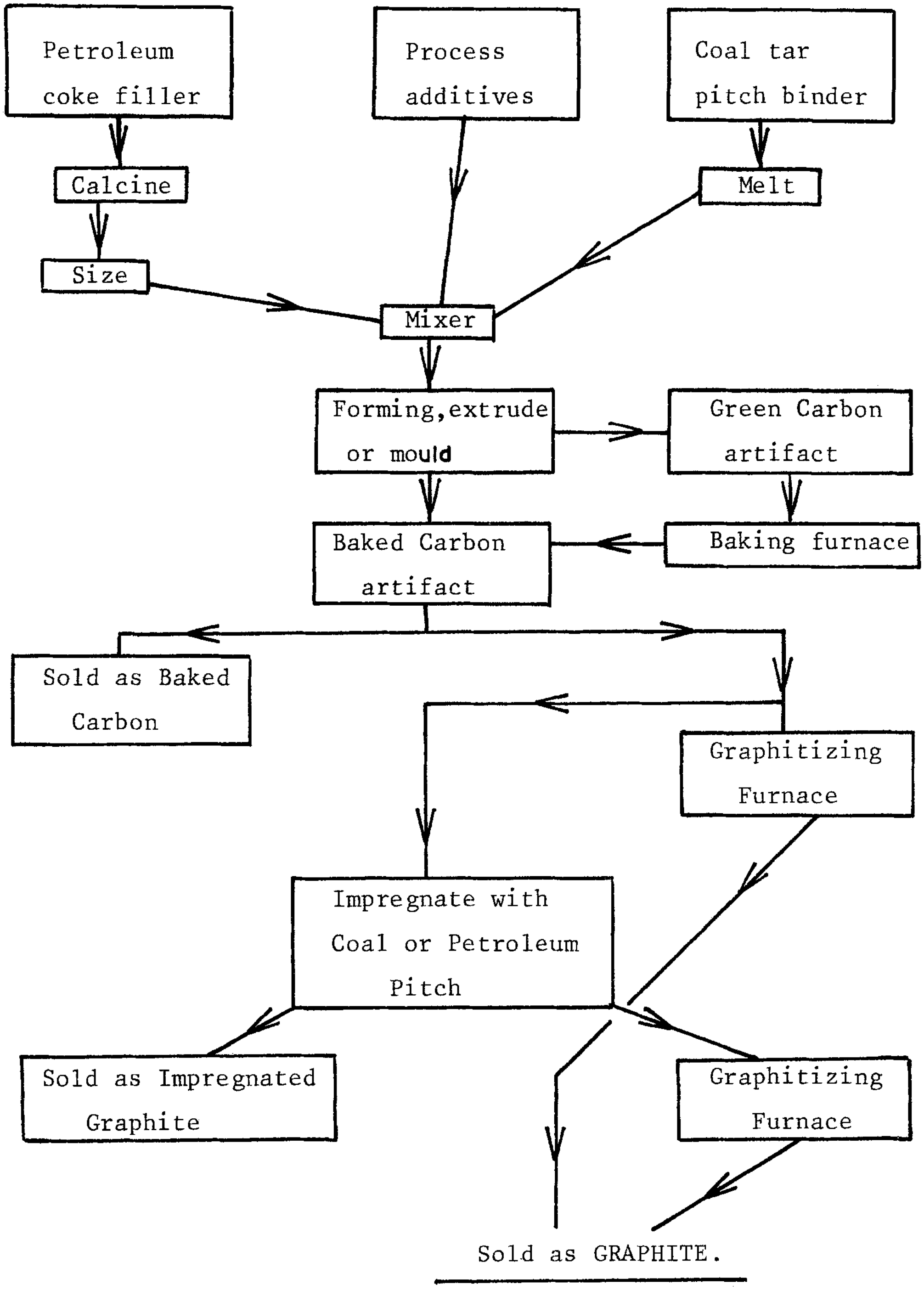

Figure 1 Typical graphite manufacturing process.

is petroleum coke made from the delayed coking process [3, 6, 7] at a production rate of ~16 × 10^6 tons per annum [8]. The range of feedstocks used for the preparation of filler coke via the delayed coking process is wide [9], the principal materials being:–

Thermal tar	Decant oil
Catalytic cracker slurry	Coal tar pitch
Ethylene cracker tar [10]	

with blends of these various types also in use [11]. This wide variation and flexibility of feedstock material makes the delayed coke process the most popular source of filler coke. Other processes are in use [8, 12, 13].

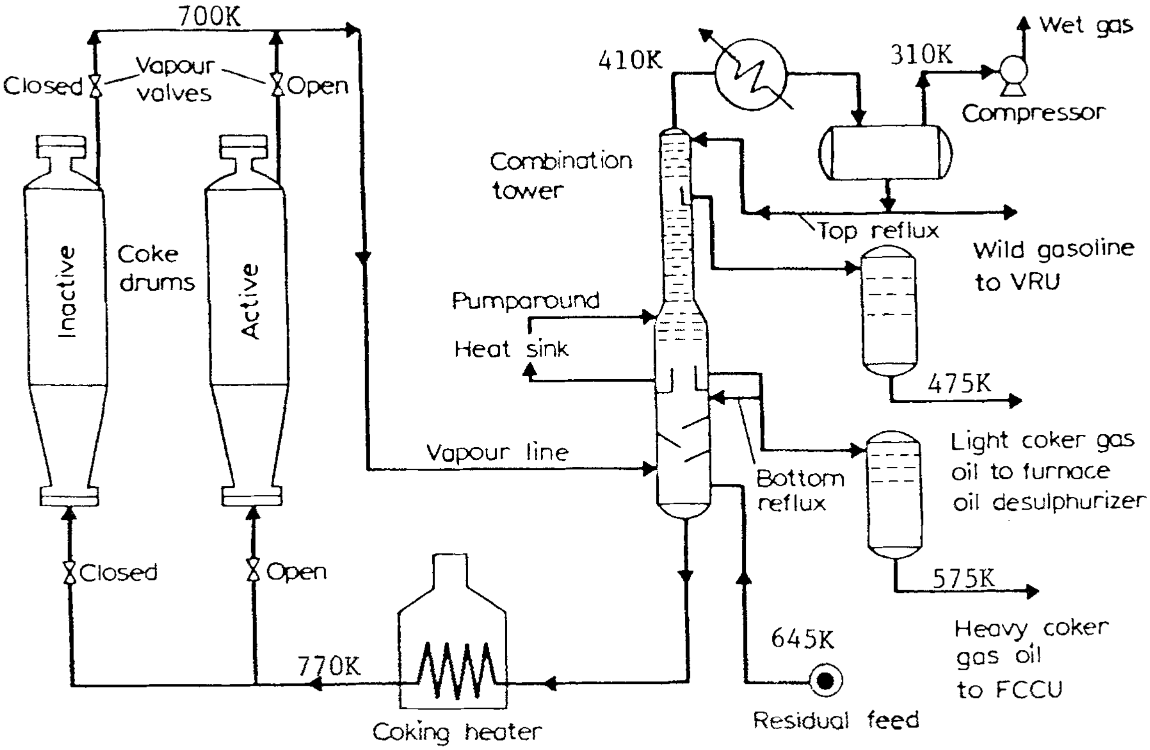

Figure 2 Schematic of the delayed coker.

Fig. 2 shows a scheme of the delayed coking process [7]. The delayed coker feed is generally the bottoms from the combination tower which is fed hot to the heater of the coker and heated to a temperature of about 770 K. The feedstock then flows into one of two coke drums where it thermally cracks to gas, gasoline, gas oil and coke [7]. The coke accumulates in the drum usually over a 24 h period while the lighter products pass back to the combination tower.

When the drum is full, the feed is switched to the second drum and quenching of the first drum commences. Early quenching uses steam, typically 900 kg h^{-1} building to 9070 kg h^{-1}, to strip out the remaining light gases and then switches to water. After a dewatering stage the cooled coke is drilled from the full drum. This drilling operation consists of drilling a pilot hole and then cutting the coke using high pressure water jets at 20 MPa. Table I summarizes a typical coking cycle.

2.1. Mechanism of coke formation

The formation of coke in the drum involves the transition of the isotropic fluid feedstock, via liquid crystals and mesophase, to optically anisotropic graphitizable carbon [14–17]. This transition of feedstock to coke begins when the optically isotropic feedstock, i.e. random relative molecular orientation [3, 14], is heated above 673 K. In this temperature range the sizes of the feedstock molecules increase as a result of polymerization [18, 19] until they are energetically favourable for the formation, by homogeneous nucleation, of lamellar nematic liquid crystals [20–22]. In the feedstock, the onset of formation of liquid crystals can be seen, via optical microscopy, as the initial formation of small (about 1 μm) optically anisotropic units which are generally spherical in form [14, 23, 24]. Once these spheres form in the bulk feedstock then either with increasing temperature, or isothermally with increasing time, the spheres enlarge at the expense of the surrounding feedstock. When two spheres meet, then coalescence is possible, but does not always occur, being dependent upon the viscosity of the system [21]. If coalescence occurs the anisotropic unit formed can regain a spherical appearance and if the conditions are favourable can even rearrange its internal structure to become a larger version of the original uncoalesced sphere. The nematic liquid crystals can be extremely fluid allowing internal arrangement to remove defects caused

TABLE I Operational cycle of a typical delayed coking unit

Operation	Description	Elapsed time (h)
Fill coke drum	Slow filling of drum with hot feed with associated coke formation.	24.0
Switch feed	Feed switched from full to empty drum.	0.5
Quench full drum		5.5
(i) Small steam	Strip remaining hydrocarbon gases and commence quenching using 900 kg h^{-1} of steam.	0.5
(ii) Big steam	Line up full drum to blow down system and commence coke cooling using 9000 kg h^{-1} of steam.	1.0
(iii) Small water	Commence quenching of coke while maintaining safe drum pressure by using 3 kg h^{-1} water.	0.5
(iv) Big water	Fully quenched coke using 60 kg h^{-1} water.	3.0
Drain drum	After water in drum stops boiling coke is cool and draining can commence.	1.5
Remove drum access heads	Top and bottom drum access heads removed so that drilling crew gain access to coke.	0.5
Cut coke		3.5
(i) Cut pilot hole	Drill out 2 m diameter pilot hole top to bottom through coke.	0.5
(ii) Coke cutting	High pressure water cutters, 20 MPa, coke discharged through pilot hole and bottom access head.	3.0
Replace access heads	Close off inactive, empty drum.	0.5
Steam and test	Check heads for leaks and purge drum of air.	0.5
Warm drum	Warm drum with vapour from active drum. Condensed vapours to fluid catalytic cracking unit.	4.0
Open vapour valve	Prepare to switch feed.	0.5
Idle time	Time allowed to slippage in other operations.	7.0

by coalescence. With continued growth of the anisotropic phase the spheres continue to coalesce but now do not regain their spherical shape, only flowing into each other and losing their individual identity. This is because viscosity increases with increasing time/temperature as a result of internal polymerization of constituent molecules. The resultant fully coalesced structure is referred to as "bulk mesophase". This bulk mesophase can still be viscous/plastic [25, 26] and will undergo further polymerization before becoming a rigid semi-coke (heat treatment temperature (HTT) $<$ 770 K) or green coke (HTT $>$ 770 K).

2.2. Coke feedstocks

The quality of the resultant delayed cokes is controlled by the chemical composition of the feedstock [5, 7, 8]. The commonly considered feedstock constituents used in feedstock classification are asphaltenes, resins and aromatics [9].

Asphaltenes from petroleum sources are considered to be colloidal dispersions of hydrocarbon molecules made up of carbon, hydrogen, oxygen, nitrogen, sulphur, vanadium and nickel in groups resembling a stack or cluster of naphthenic and aromatic molecules with typical molecular weights between 3000 and 5000 amu [27, 28]. Resins are similar to asphaltenes but are lighter with molecular weights 200 to 300 amu less than the corresponding asphaltenes [29]. Aromatics are composed of polycyclic six carbon atom rings which are unsaturated but very stable. Paraffinic and naphthenic molecules, although very different chemically and physically from aromatic hydrocarbons, [30], are often included in the "aromatic" group.

Coking of feedstocks with high concentrations of asphaltenes and resins produces a highly cross-linked coke with a high concentration of impurities, e.g. sulphur and vanadium, making such coke unsuitable as filler coke [9]. Feedstocks with higher contents of "aromatic" molecules, e.g. vacuum residues with about 50 wt % aromatic carbon [31], produce filler coke suitable for baked aluminium electrodes [3, 7, 8]. Coking of feedstocks with very high concentrations of aromatic carbon, e.g. decant oils or ethylene cracker tars with > 70 wt % aromatic carbon [32, 33] produces a high quality readily graphitizable coke known as needle-coke. This coke, after calcining, is particularly suitable as filler coke for ultra-high potential graphite electrodes [3, 8].

Although feedstock characteristics are without doubt held to be dominant in determining the properties of the resultant green cokes [7, 9], variation in operation of the delayed coker can produce some variations in the quality of green coke from a particular feedstock [7, 34]. Longer filling times, (coker dwell time) may produce hard green coke which proves difficult to cut at the end of the coking cycle. Also, low coking temperatures produce green cokes with high volatile matter contents known as soft cokes.

3. Calcining of delayed cokes

Green coke is generally considered unsuitable as filler coke because of its tendency to shrink upon heat treatment [3, 35]. However, some special grade graphites use green coke as filler [36]. The amount of shrinkage of green coke upon heat treatment is related to its volatile matter content [35]. Because of this shrinkage, green coke is generally heat treated prior to its use as filler, the process being known as calcination (1–3).

Green coke has between 5 to 15 wt % volatile matter and when calcined to 1700 K it shrinks to about 10 to 14% [3]. During calcining the volatile matter content is reduced to about 0.5%, the volatiles being released as gases, principally CH_4, C_2H_6, H_2, H_2S and CH_3SH [9]. These are burned during calcining to provide much of the process heat. To prevent partial fusion of the coke during calcining, the volatile content of the green coke is kept below a few wt % [3]. The selection of calcining equipment depends upon the temperatures required. Three major calciner units are used for cokes; the horizontal rotary drum/kiln similar to that used for calcining limestone, the vertical rotary hearth and the vertical shaft type, with the rotary kiln being the most widely used.

3.1. Rotary kiln calciner

The widespread use of the rotary kiln results from such kilns being readily available, simple in design and fabrication with the potential for high throughput. Fig. 3 shows a typical flow chart for a rotary kiln calciner. However, such kilns have the following disadvantages:

(a) Care must be taken in firing the units to prevent damage to refractories and kiln shell.

(b) Costly maintenance of the refractory lining of the kiln caused by its abrasion by the moving coke.

(c) Petroleum coke dust or fines which are relatively abundant in the green coke feed are readily entrained in the hot gases moving over the coke bed.

(d) Relatively high loss of process heat.

(e) Coke throughput and residence time are fixed by the rotation rate and shape of the kiln.

Handling and conserving of coke fines is the major problem associated with processing in rotary kiln calciners. The fines are readily entrained by the relatively high velocity gas stream flowing up the kiln because of the cascading action within the kiln. This thereby constitutes an air pollution problem if they are not removed. In addition they can represent a loss of valuable carbon amounting to as much as 4 to 5% of the total carbon charged to the kiln [37]. The mechanical loss of fines occurs in addition to the carbon burned in the kiln itself by contact with combustion air and other oxidizing gases, e.g. water vapour and carbon dioxide. The extent of combustion loss is not well defined and apparently varies from kiln to kiln depending upon operating conditions, i.e. amount of excess air, kiln firing temperature, residence time and off-gas temperature. However, total carbon losses (mechanical and combustion) amount to 12 to 15% of the fixed carbon charged to the kiln [37, 38].

3.2. Rotary hearth calciners

Noting the recognised shortcomings of the rotary

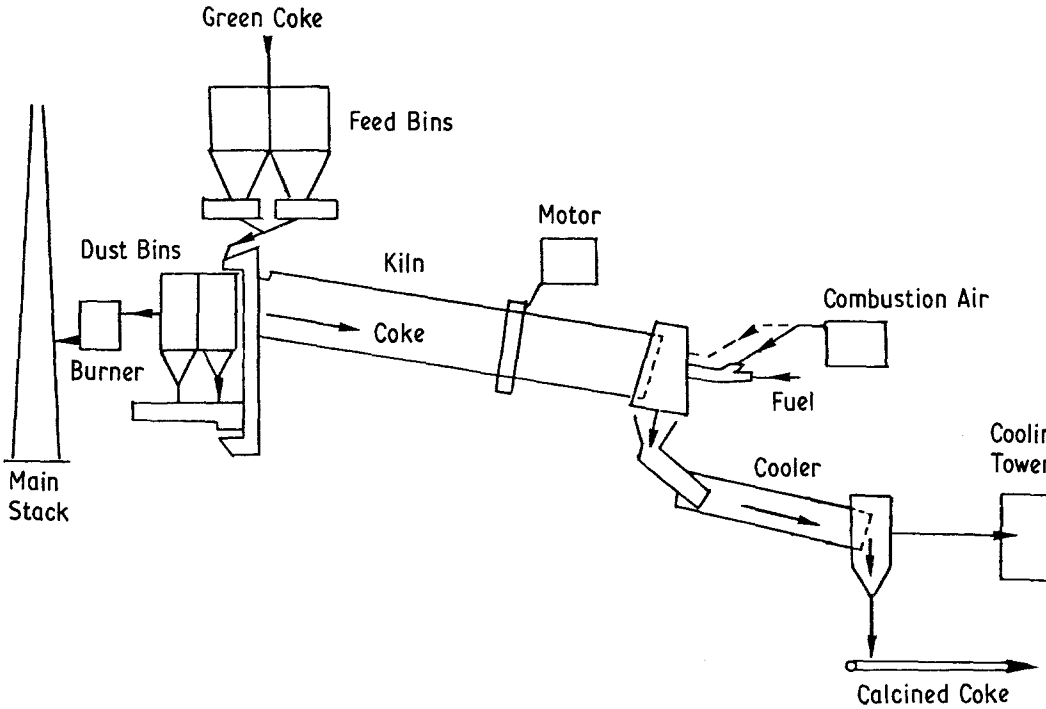

Figure 3 Schematic of a rotary kiln calciner.

kiln, recent calciner installations in Europe have tended toward the use of a rotary hearth type calciner [38] originally developed by the Wise Coal and Coke Company [39]. Fig. 4 shows a simplified flow sheet for a rotary hearth calciner and auxillary units. Fig. 5 shows an elevation of the rotary hearth calciner. Green coke charged at the periphery of the hearth travels around the calciner in a series of concentric paths. At the completion of each revolution the coke is moved, via a rabble arm set in the roof, into the next concentric path. This process is repeated until,

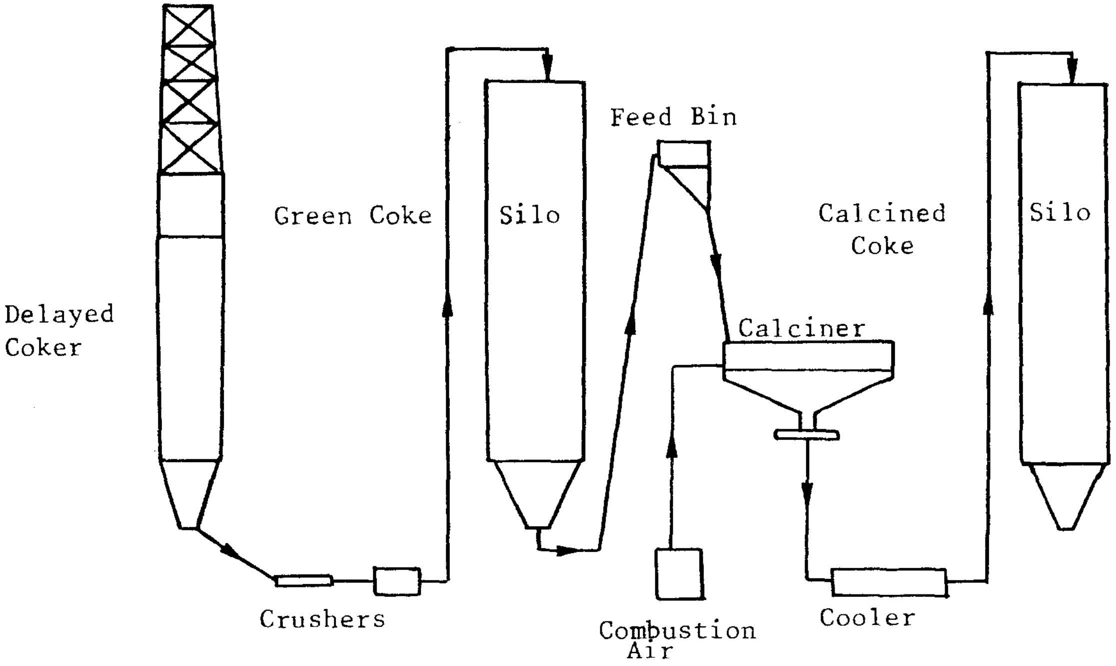

Figure 4 Schematic of a rotary hearth calciner.

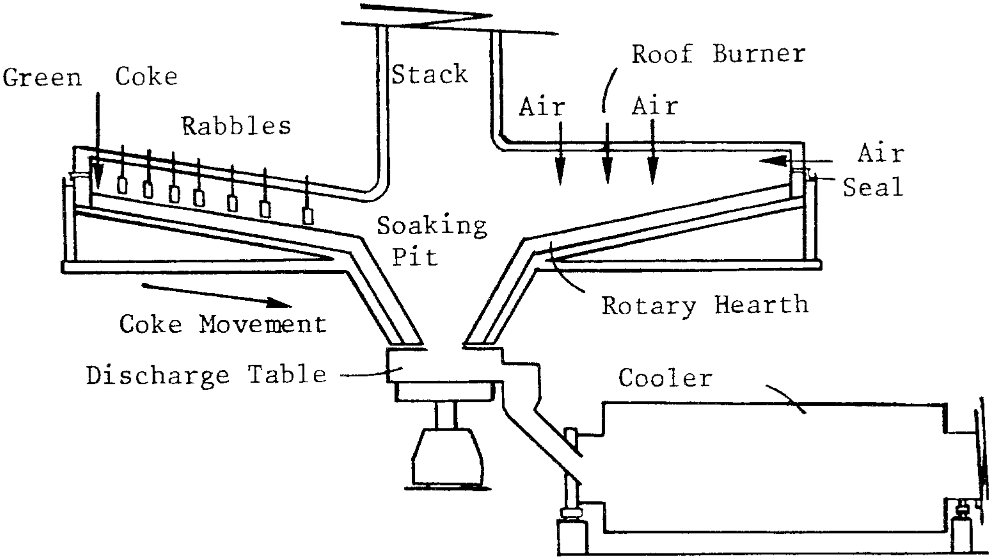

Figure 5 The rotary hearth calciner.

at the final rabble, the coke is discharged into the soaking pit. From the soaking pit the coke may be discharged to the cooling drum. During normal operation the retention time for the coke in the hearth is approximately 1 h.

In addition to moving the coke from feed point to the discharge, rabbling provides the characteristic advantages of the process, e.g.

(a) It gently stirs the coke bed without mechanical attrition which occurs from the cascading action within a rotary kiln.

(b) The fines work into the coke bed and are not swept into the off-gas stream.

(c) Heat transfer is enchanced by continuous exposure of new surfaces toward the hot radiating arch above the bed.

The heat required for calcining the green coke is primarily provided by burning the volatile matter released from the coke during the calcining process, Fig. 6. Combustion air is admitted to the calciner through a series of ports uniformly spaced around the periphery and roof of the calciner. The total air input is controlled via gas analysers in the stack of the calciner. Normal operation admits sufficient air for complete combustion of the volatiles released from the coke, i.e no free oxygen in the off gas. However, it is normal practice to admit excess air to control the temperature of the hearth and this may lead to combustion of the coke bed. Combustion may adversely effect the properties of the resultant calcined coke as well as reduce the yield of calcined coke from the unit [40] which is typically 93% of the fixed carbon charged.

3.3. Vertical shaft calciners

Vertical shaft calciners are essentially counterflow solid–gas reactors in which the green coke is heated as it descends under gravity by recycled, pre-heated volatiles released by green coke calcined earlier. The heating of the volatiles occurs either by combustion in a tuyere beneath the calciner or by direct electric resistance heating of the calciner walls and then via conduction and convection to the green coke [41]. Early shaft calciners were similar to coal-coke ovens with the side walls of the calciner being heated via external firing of the volatiles released from the green coke [1].

Although shaft kilns eliminate the problems of mechanical and combustion carbon loss and are cheap to install and maintain, their low throughput, typically only 2.5 ton h^{-1} [42] against 15 ton h^{-1} for a rotary hearth [43] has limited their use. Such kilns have proved particularly useful in the calcining and desulphurizing of petroleum cokes with high sulphur contents, i.e. >4 wt% [41], and in the calcining of anthracite, calcining temperature 2273 K, for production of carbon refractories [3].

3.4. Specifications of delayed coke

Following calcination the delayed coke is now acceptable as a filler coke. Table II shows typical

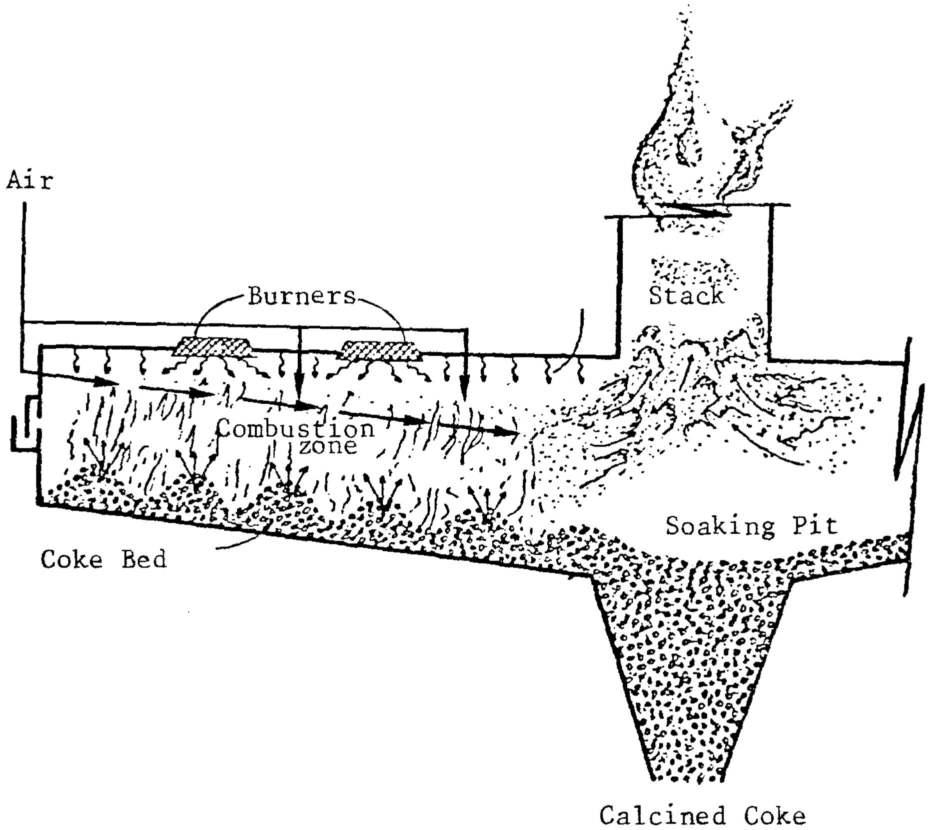

Figure 6 Volatile matter combustion in the rotary hearth calciner.

specifications of sponge coke, for use in aluminium anodes, and needle-coke for use in graphite arc electrodes. In the manufacture of aluminium, undesirable impurities are vanadium, nickel, iron and silicon; hence low ash contents are important in sponge cokes [7]. Impurities such as sulphur are less important. However, environmental protection legislation in the US may force aluminium manufacturers to adopt a < 1 wt % level for sulphur specification [44]. In the manu-

TABLE II Typical properties of sponge and needle-cokes

Property	Aluminium anode grade sponge coke		Graphite electrode grade needle-coke	
	Green	Calcined	Green	Calcined
Carbon (wt %)	86–95	98–99.6	90–95	98–99.6
Volatile Matter (wt %)	10–12	2.5 max	8.0	< 0.5
Sulphur (wt %)	2.5	< 1.0	1.0	0.9
Ash (wt %)	0.25	0.50	0.10	0.15
Silicon (wt %)	0.02	0.02	0.04	0.04
Vanadium (ppm)	150	200	2.0	2.0
Nickel (ppm)	150	200	20–40	20–40
Iron (ppm)	50–2000	50–2000	–	–
Manganese (ppm)	2.0–100	2.0–100	–	–
Resistivity (ohms m^{-2}) (– 35, + 65, Tyler mesh, i.e. < 490 μm, > 230 μm)		890		965
Real density (kg m^{-3})	1.6–1.8	2.06	1.6–1.8	2.14
Bulk density (kg m^{-3})	–	0.80	–	0.90
Coefficient of thermal expansion (K^{-1}) (300 to 473 K)	–	20 × 10^{-7}	–	5 × 10^{-7}

TABLE III Analyses of coal tar and coal tar pitches

	Coal tar	Medium pitch	Electrode pitch
Density at 293 K (kg m^{-3})	1.18	1.28	1.32
Softening Point (K) (Kraemer–Sarnow)	< 273	341	365
Softening Point (K) (Mettler)	< 273	359	383
Quinoline insolubles (wt %)	3	7	14
Toluene insolubles (wt %)	8	18	39
β-resins (wt %)	5	11	25
Carbonization residue (wt %)	20	45	60
Carbon (wt %)	91	92.5	94
Hydrogen (wt %)	5	4.5	4.3
C/H ratio	1.5	1.7	1.8

facture of graphite electrodes low sulphur specifications for the needle-coke fillers are important as, on graphitization, fillers with high sulphur contents, i.e. > 0.8 wt % [43], swell due to the elimination of the sulphur as a gas. This swelling, known as puffing, may cause fracture of the graphitizing artifact [1–3, 43], and at the very least generally degrades properties.

4. Grinding and sizing of calcined cokes

The calcined coke filler is usually supplied to the graphite manufacturer in particle sizes ranging from fines to 5 to 8 cm diameter pieces. Hence, the first stage in the manufacture of the graphite is the crushing, sizing and milling of the calcined coke. The degree to which the calcined coke is broken down depends upon the grade of graphite to be made [2, 3]. If the product is to be fine-grained for nuclear, aerospace or metallurgical application, then milling and pulverizing are necessary to produce filler particles a few microns in diameter. However, if the product is to be coarse in character, e.g. aluminium anodes, etc then high yields of particles up to 1.3 cm are required [3] and simple crushing may suffice.

There are three main principles to be considered when selecting a filler size distribution [2]. The first is the reduction of voidage by packing of small particles into the interstices between larger particles [45]. The second, and opposing principle, is to provide enough porosity to allow the volatile pyrolysis products from the binder phase to escape during the baking operation. Thirdly, there is the need, in special applications, to control the size distribution of the porosity in the final product as well as the total amount. These conflicting requirements are often resolved by control of the size ratios of the filler particles required by the 1st and 3rd principles, while the absolute size of the coarsest particle is increased in proportion to the size of piece being baked. Typical particle size distributions of various filler systems have been published [1, 46].

The shape of the particles as well as their size have been found to be significant [2]. Particle shape affects packing, the orientation of the filler particles during manufacture and hence the degree of isotropy of the properties of the final product. The shape of the filler particles has been found to depend upon the initial size of the coke particles and upon the type of filler coke, particularly the extent of micro-crack formation within the coke on calcining [47].

5. Binder pitches

Carbon artifacts are manufactured by mixing a controlled size distribution of filler particles with a binder phase, typically a pitch. The function of the binder pitch is to plasticize the filler powder so that it can be formed into bodies of the required shape or size which are strong enough to withstand handling in the later stages of manufacture. Subsequently, the binder must carbonize in good yield forming a coke that bridges the filler particles providing a strong, dense, artifact with suitable thermal and electrical conductance.

Binder specifications vary with the specifications of the carbon article required. Binders used in the manufacture of electrodes and graphite products need to fulfil the following specifications [3]:

(a) High carbon yield, usually 50 to 60 wt % of pitch.

(b) Show good wetting and adhesion properties to bind together the filler particles during manufacture.

(c) Exhibit suitable softening behaviour at mixing temperatures usually in the range 410 to 460 K.

(d) Contain only minor amounts of mineral and extraneous matter that could reduce strength and other physical properties.

(e) Produce a graphitizable binder coke to improve electrical and thermal properties.

(f) Be of low cost and wide availability and to be consistent from batch to batch.

The preferred binder is coal tar pitch from the high temperature destructive distillation of bituminous coal (coking). Table III shows the typical analyses of a straight run medium coal tar pitch and electrode binder pitch [8]. The composition of the straight run medium pitch in terms of β-resins (i.e. soluble in quinoline, insoluble in toluene) and coke yield varies with the properties of the crude tar. For the production of a good binder pitch it is advantageous to treat the medium pitch in a thermal reforming step after the initial distillation. The thermal treatment at 1.5 MPa pressure leads to an increase in β-resins and QI (quinoline insolubles). Further adjustment of softening point, ratio of inherent/secondary QI and Conradson coking residue can be carried out during flash distillation of the thermally treated medium pitch by varying temperature, pressure and soak time [8].

Various attempts have been made to circumvent this thermal reforming stage by oxidizing the pitch with air or by the addition of carbon black or mesophase (quinoline insoluble) to the pitch, effectively raising the carbon yield and QI levels [48]. However, such modified pitches have not proved satisfactory binders as the additives do not wet the filler particles and hence contribute nothing to the binding ability of the pitch [2, 8]. Additions of sulphur or nitro-aromatic compounds increase the carbon yield on baking but adversely affect the graphitizability of the binder [49–51].

Although coal tar pitch is the main source of binder pitch, other sources are becoming increasingly important. Chief among these other binders are petroleum pitches which, if produced from the proper charging stock, have proved adequate binders for aluminium anodes [52]. Synthetic resins, notably furfuryl alcohol and polyfurfuryl alcohol, have also been examined as binders [53, 54] and have proved useful in the production of high density graphites used in special grades. But such additives increase resistivity.

5.1. Additives to the mix

In addition to the primary raw materials in the mixes (filler and binder) minor amounts of other materials are added at various steps in the process. Although the amounts of these materials are small, they play an important role in the economic manufacture of the final product [1].

Light extrusion oils and lubricants, e.g. anthracene oil, are added to the mix to improve extrusion rates and the structure of extruded products. Inhibitors are added to reduce the detrimental effects of sulphur in high sulphur filler cokes. Iron (II) oxide is added to such cokes to prevent puffing the mechanism being the formation of a stable sulphide so reducing the pressure of sulphur-containing gases in the graphitizing matrix. Other sulphide forming elements such as sodium, nickel, cobalt and calcium may be used.

6. The manufacturing process

6.1. Mixing

Once the raw materials have been crushed and sized the manufacturing process begins with a mixing operation which blends the filler with molten binder pitch and coats the grains of filler coke with binder. The intergranular bond (whatever its nature) ultimately determines the structural integrity of the graphites. Thus, the more uniform the binder distribution throughout the filler coke, then the greater the likelihood of a structurally strong product [3].

Mixing is normally performed in kneader-type equipment although twin screw mixers are used for fine-grained products [3]. All mixes are heated so that the binder is fluid. The intensity of the mixing is normally low to avoid filler breakage. The proportions of the mix are normally chosen so that, at the next stage of manufacture, the system contains sufficient binder to exclude air from the interstices between the particles. In calculating this amount, allowance must be made for penetration of binder into porous filler particles. Also, during the forming stage, the mix will be compacted and will require less binder than during mixing. These requirements result in a typical mix composition containing 20 to 75% of binder.

Following the mixing operation the hot mix, typically at 460 K at the discharge point [3], must be cooled to slightly above the softening point of the pitch. The cooled mix, typically 390 to 400 K, has the correct rheological properties for the forming operation and is better able to maintain its shape on cooling to room temperature. The total mixing time, mixing and cooling, is typically 1.25 h.

6.2. Forming

The primary purpose of the forming operation is to increase the density of the mix. This results in intimate contact between the pitch coated filler particles, a major reduction in porosity of the mix and the production of a green artifact with a size and shape as near as possible to the finished article so minimizing machining and finishing costs. Two principal methods of forming exist, i.e. extrusion and moulding.

6.3. Extrusion

The extrusion process is used to form most carbon and graphite products. The various extrusion techniques comprise a removable die attached to a hollow cylinder known as a mud chamber. The cylinder is charged with mix that is extruded in a number of ways dependent on the press design. In one type of press the cooled mix is charged to the mud chamber in the form of pre-moulded plugs. A second type of extruder, popular because it removes the need for pre-moulded plugs, and known as the tilting press, has a movable mud chamber which is charged with mix, via a vacuum tamping hammer, in the vertical position. The mud chamber then tilts to the horizontal position and the mix is extruded through the die. A third type of extrusion press uses an auger to force the mix through the die. This type of press is used principally with fine-grained mixes because of its tendency to fracture larger filler particles.

After extrusion, a guillotine knife located at the die outlet cuts the extruded product to the desired length. Cylindrical products are rolled into a tank of water and cooled quickly to prevent distortion of the plastic mix called "slumping". Products with rectangular cross-sections may be moved to a cooling bank by crane [3]. Water temperatures must be regulated to avoid cracking caused by rapid cooling. Products with small cross sections, such as anodes for chlorine cells, may be cooled in air or with a water mist.

The extrusion process produces a bulk anisotropy in the resultant artifact and graphite. During extrusion the filler particles align with their long dimensions parallel to the extrusion direction. The most important factors controlling the development of this bulk anisotropy are filler type, particle size and the ratio of the die to mud chamber diameters during extrusion. The more needle-coke like are the filler cokes then the greater is the observed anisotropy in properties between the with-grain and cross-grain directions because of the predominance of lath-shaped particles when such cokes are ground. The use of fines in the mix also increases anisotropy as they more readily align than do large particles during extrusion. As the ratio of mud cylinder to die diameter increases, so does the degree of anisotropy. As a result of particle orientation, extruded graphitized products possess values of compressive and tensile strength, Young's modulus and thermal conductivities which are greater in the with-grain direction than in either cross-grain directions. Values of electrical resistivity and coefficient of thermal expansion are smaller in the with-grain direction (parallel to extrusion) than in either cross-grain directions.

6.4. Moulding

Moulding 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 moulding carbon artifacts. The presses may be single- or double-acting, dependent on whether one or both platens move to apply pressure to the mix through punched holes in either end of the mould. 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 mould wall. Acceptable thickness of moulded artifacts can be increased by using double-acting presses which apply pressures equally at the top and bottom of the product.

Jar moulding is another method used to increase the length of the moulded piece and keep variations of properties within acceptable limits. By this technique the heated mould 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 moulded in this way; the green densities are comparable with those obtained in extruded artifacts.

The cooling step for pieces of large size is the most critical part of the forming operation. Because of the low thermal conductivity of pitch, $0.13\,\mathrm{Wm^{-1}\,K^{-1}}$ [55], and its relatively high expansion coefficient ($4.5 \times 10^{-4}\,\mathrm{K^{-1}}$ at 300 to 570 K) [56], stresses build rapidly as the outer portions of the piece solidify. If cooling is too rapid, internal cracks are formed which 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 mould for specified time periods.

When the outside of the piece has cooled sufficiently, it is stripped from the mould and the cooling operation continued by direct water spray or under pressure. If cooling is stopped too soon, heat from the centre 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 which may result in temperature gradients and damage to the structure. Bulk density of the green artifact is usually 1.65 to $1.70\,\mathrm{kg\,m^{-3}}$ as against 1.75 to $1.80\,\mathrm{kg\,m^{-3}}$ for extruded green artifacts.

As with extruded artifacts, moulded pieces have a preferred grain orientation. The coke particles are aligned with their long dimensions normal to the moulding direction. Thus, the moulded product has two with-grain directions and one cross-grain direction which coincides with the moulding direction. Strength, Young's modulus and conductivity of moulded graphites are higher in both with-grain directions and the expansion coefficient is higher in the cross-grain direction [3].

6.5. Baking

The next stage in the manufacture of graphite is baking during which the green artifact is heated to 1073 to 1273 K. One function of this step is to convert the thermoplastic pitch binder to solid coke. Another function of baking is the removal of the shrinkage in the artifact 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 and, 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 the weight loss and volatile evolution as functions of temperature [57]. During this process weight losses of 30 to 40% occur indicating that for every 500 kg of green mix containing 30% binder, 45 to 60 kg of gas must escape. In terms of gas volume, approximately $150\,\mathrm{cm^3}$ of volatiles as standard conditions must be evolved per gram of pitch binder during the baking operation. The artifact 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. If heating rates exceed a critical value, normally in the range 2 to $10\,\mathrm{K\,h^{-1}}$ dependent upon size and composition of the artifact, then 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 artifact in the 480 to 680 K range where the pitch binder is in a liquid state. To prevent slumping and distortion during this period, the artifact must be packed in carefully sized coke or sand which provides the necessary support and is sufficiently permeable to vent volatiles from the binder pitch.

A variety of baking furnaces provide the flexibility needed to bake a wide range of product sizes and to generate the best possible temperature control. However, most baking furnaces are variations on the pit furnace, so named because the furnace is positioned partly or totally below ground level. In essence, the pit furnace is a box with ceramic brick walls containing ports or flues through which hot gases circulate [3].

Firing schedules vary being dependent upon artifact size and shape, type of furnace used and binder content of the artifact. A typical pit furnace packed with 0.6 m x 0.8 m x 4.6 m pieces of speciality graphite may require up to 6 weeks to fire and 4 weeks to cool. However, electrodes generally require 2 weeks to fire and 5 days to cool [3]. Most carbon products have unpacking temperatures below 680 K to avoid cracking due to thermal shock.

After cooling, the baked carbon or artifact is cleaned, weighed and measured before being stored prior to further processing. Some artifacts are sold in the baked state after machining particularly aluminium electrodes and blast furnace refractories.

6.6. Impregnation

In some applications the baked artifact is taken directly to the graphitizing facility for heat treatment. However, in the manufacture of high performance graphites an impregnation stage is used before final graphitizing so as to reduce porosity and increase the density of the final graphite. Such impregnation stages may be repeated following each re-bake; however the improvements in properties decrease as the quantity of impregnant taken up in each succeeding impregnation also decreases.

During the baking stage, binder pitch exuding from the artifact surface creates a dense impermeable skin. In addition, the exuded pitch causes packing material to adhere to the baked artifact. The skin and the packing material must be removed by sanding, scraping, or machining before the artifact can be impregnated on a reasonable time cycle. Unless this operation is properly performed, the impregnant may not reach the centre of the product and a so-called dry core will result. When this condition exists, the artifact usually splits during graphitization as a consequence of the greater concentration of pitch and greater shrinkage in the outer portions of the artifact.

The likelihood of a dry core increases with increasing quinoline-insoluble solids content of the impregnant. This is because during impregnation processes, the insolubles form a filter cake of low permeability on the artifact surface, reducing the penetrability of the impregnant. Quinoline insoluble contents significantly greater than 3% reduce the penetration rate and increase the incidence of dry cores [3]. Hence petroleum pitches or coal tar pitch with 0% QI are used in pressure impregnation.

Although the impregnant is usually a low melting point petroleum or coal tar pitch, impregnation using liquids which pyrolyse, without fusion, to non-graphitizable carbon leaves a fine, predominantly closed porosity in the final graphite. This type of impregnant is therefore particularly suitable in the reduction of permeability without increasing density. Furfuryl alcohol [58], sugar [59] and divinyl benzene [60] have been used. Impregnation using hydrocarbon gases which are then thermally cracked to produce pyrolytic carbon within the artifact could be attractive. However, it has proved difficult to apply this idea to large artifacts as cracking at the entry of pores hinders subsequent access of the impregnant gases.

6.7. Graphitization

Graphitization is an electrical heat treatment of the baked artifact to about 3300 K. The heat treatment, in simplistic terms, causes movement of the carbon atoms in the baked carbon composite to the thermodynamically more stable graphite lattice.

The furnace that made the graphite industry possible was invented in 1895 by Acheson [61] and is still in use today with only minor modifications. It is an electrically-fired furnace capable of heating several tons of charge to temperatures approaching 3300 K. The basic elements of the Acheson furnace consist of a furnace bed which is made up of refractory tiles supported by concrete piers. The furnace ends are U-shaped concrete heads through which several graphite electrodes project into the pack. These electrodes, which are a 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.

Any artifact shape can be graphitized in the Acheson furnace as long as the product pieces are carefully spaced. This feature of the Acheson furnace makes it extremely versatile. With the product in place, a coarsely-sized metallurgical coke, called resistor pack, can be 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 to 1 m from the charge ends, are used to retain the insulation. The procedure for loading a furnace usually requires one day [2, 3]. Longitudinal graphitization is preferred by some manufacturers.

Normal operation of these furnaces utilizes heating rates of 40 to 60 $\mathrm{K\,h^{-1}}$, a total firing time of approximately 3 days and a final graphitizing temperature of 3000 to 3300 K. Following the heating cycle, cooling and unloading of the furnace takes a further 8 to 10 days. Cooling is hastened by the gradual removal of the resistor pack but care must be taken so that sufficient pack remains to prevent oxidation of the graphitized artifacts. When cooling is complete, the product is unloaded, cleaned and inspected prior to assessments of bulk density and resistance of product. When properties are within specified limits, then the graphitized artifacts are stored prior to final machining [3].

The process of graphitization essentially is the development of an ordered crystallographic structure from an initial relatively partially disordered graphitizable carbon. Initial concepts of the development of this crystallographic ordering envisaged graphitization as an annealing of small scale disordered stacks of graphitic atomic layers to the large scale crystallographically perfect structure [62]. However, modern concepts of the graphitization process suggest continuous increases in perfection of crystallographic ordering as the result of the initial elimination of molecular side chains, i.e. coking, in the temperature range 700 to 1000 K, followed by an increasing extent and perfection of ordering resulting from elimination of heteroatoms, e.g. hydrogen, sulphur, etc. and an annealing of interlayer defects, in the range 1000 to 3000 K [63, 64]. Industrial graphitization does not result in single crystal graphite. Hence gross structures, e.g. optical texture, developed by the filler and binder phases remain after graphitization, ultimately controlling the properties of the graphite.

7. Advanced processing technology

The previously outlined manufacturing process has been successfully used in the production of graphite without change for almost a century. However, recent demands for high density graphites with isotropic bulk properties and the economic advantages of shortening graphite manufacturing times have led to the development of more advanced manufacturing techniques. The areas of the manufacturing process which have received most attention have been the forming and impregnation stages.

7.1. Isostatic hot pressing

Originally developed at Battelles' Columbus Laboratories in the USA [65] isostatic hot pressing has been developed into commercially viable techniques for the fabrication of high density speciality graphites [66]. Essentially the isostatic hot pressing technique is a high temperature, high pressure compaction process. The filler/binder mix is encapsulated in a hermetically sealed metal container and placed in an autoclave. When the container is heated the pressure in the autoclave increases and at high temperatures the container becomes plastic so transmitting the full autoclave pressure to the mix. Consequently the mix is triaxially compressed and this results in a large increase in density.

7.2. Artifact densification

The production of densified artifacts is essentially identical to the isostatic hot pressing technique except that the charge in the autoclave is a preformed solid prior to pressing [67]. The charge may be a graphitized or baked artifact. Also, the technique differs from the isostatic hot pressing in requiring very high temperatures, i.e. 2500 K, to produce plastic deformation of the solid carbon. Once such temperatures are reached triaxial compression of the artifact occurs and very high densities of products are obtainable for special grades only [67].

7.3. High pressure impregnation/baking

A further application of isostatic pressing technique has been the incorporation of the impregnation and baking stages into the same process operation. The porous, preformed artifact is charged to a steel container and subject to a conventional atmospheric pressure impregnation. The impregnated artifact is then hermetically sealed in a process container and isostatically hot pressed or baked at temperatures of 1000 K and pressures of 100 MPa. Baking under such conditions results in a 91 wt% binder coke yield and the technique is reported for densification of carbon–carbon composites used as re-entry heat shields for spacecraft [67].

7.4. Binderless graphites

The application of hot pressing techniques at very high temperatures and pressures, i.e. 3000 K, 120 MPa, to artifacts pre-formed from filler coke without a binder phase, yields very high strength, high density graphites known as binderless graphites [67]. However a "binder" is generally the coke precursor dissolved in an organic solvent using ultra fine-grained green coke as the filler. The solvent is boiled off in the moulding press and the artifact is cooled under pressure.

Although both graphite and coke particles have been used as the filler phase in the production of binderless graphites, coke filler fines, i.e. particles size $\simeq 25\,\mu$m, have been found to produce a superior binderless graphite. This results from their partially graphitized structure with its high density of mobile defects being more readily sintered. Low temperature petroleum cokes, i.e. green coke at about 800 K, although easily sintered, may prove unacceptable for binderless processing due to excessive shrinkage on graphitizing [68].

Binderless graphites are processed at temperatures from 2000 to 3000 K and at pressures from 100 to 200 MPa with the highest strength graphites being obtained at the higher temperatures. Selection of encapsulating material is difficult with tantalum being most widely used due to its high carbide eutectic temperature (3100 K). However, tantalum reacts readily with sulphur at temperatures above 1800 K so that very low sulphur cokes, i.e. < 0.5 wt% [67] should be used.

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