Graphite production
&
further processing

Graphite blocks

Graphite production & further processing

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- Coating
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Some applications, such as graphite electrodes for the electric arc furnace require a higher thermal and electrical conductivity than that of baked carbon materials. These synthetic graphites normally follow a production process similar to that of baked carbon (forming, impregnation, rebaking) but require an additional process step, that of graphitisation where temperatures of around 3000°C are achieved.

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Heat treatment - graphitising

The final step in graphite manufacture is a conversion of baked carbon to graphite, called graphitising, i.e. heat-treating the material at temperatures in the region of 2600°C – 3300°C. During the graphitising process, the more or less pre-ordered carbon (turbostratic carbon) is converted into a three-dimensionally ordered graphite structure. Depending on the raw materials and the processing parameters, various degrees of convergence to the ideal structure of a graphite single crystal are achieved.

Since graphitisation increases the lattice order and produces smaller layer distances, it simultaneously leads to a considerable growth of ordered domains. However, the degree of order that can be reached depends largely on the crystalline pre-order of the solid used. These reduced lattice layer distances are macroscopically noted as a contraction in volume. This graphitisation-shrinkage is approximately 3 to 5%. Due to this shrinkage, density of the graphite increases.

the process

General: The Graphitisation Process

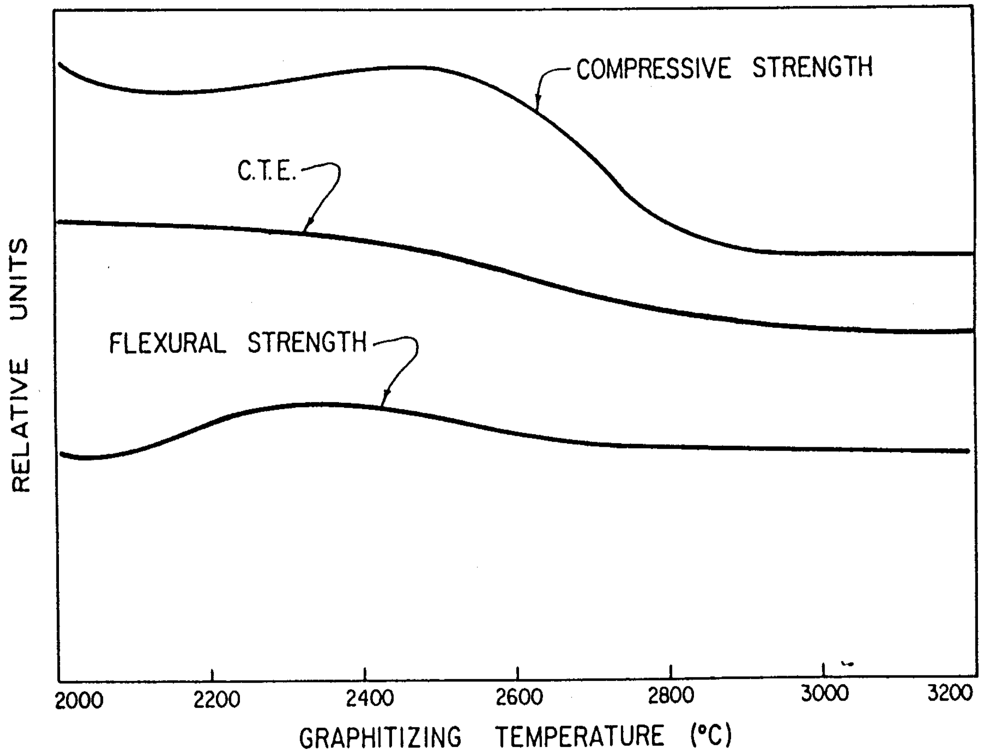
- The final step in the production of graphite is the graphitisation process.
- Amorphous or baked carbon is converted to electrographite
by a thermal treatment at approximately 3000°C.
- Essentially any amorphous carbon material can be graphitised.
The potential crystallite growth and ordering are latent within the baked carbon structure.
- Under the influence of temperature the crystallites grow and rearrange
in an ordered pattern of stacked parallel planes.
This transformation is accompained by a change in the physical properties of the material
(See change during graphitisation).
- The greater the degree of crystallite growth during heating up, the better the graphitability
(gaphitization degree), which effects the final resistivity achieved.
- There is a variation among different needle cokes concerning the graphitability.
- The graphitisation degree depends on the structure of the basic material (graphitability)
and the applied graphitisation temperature.
It is determined by x-ray measurements.

Changes during graphitisation

1. Crystal development
2. Material gets softer and machinable
3. Impurities vaporize
4. Becomes a better electrical and thermal conductor
5. Physical property changes

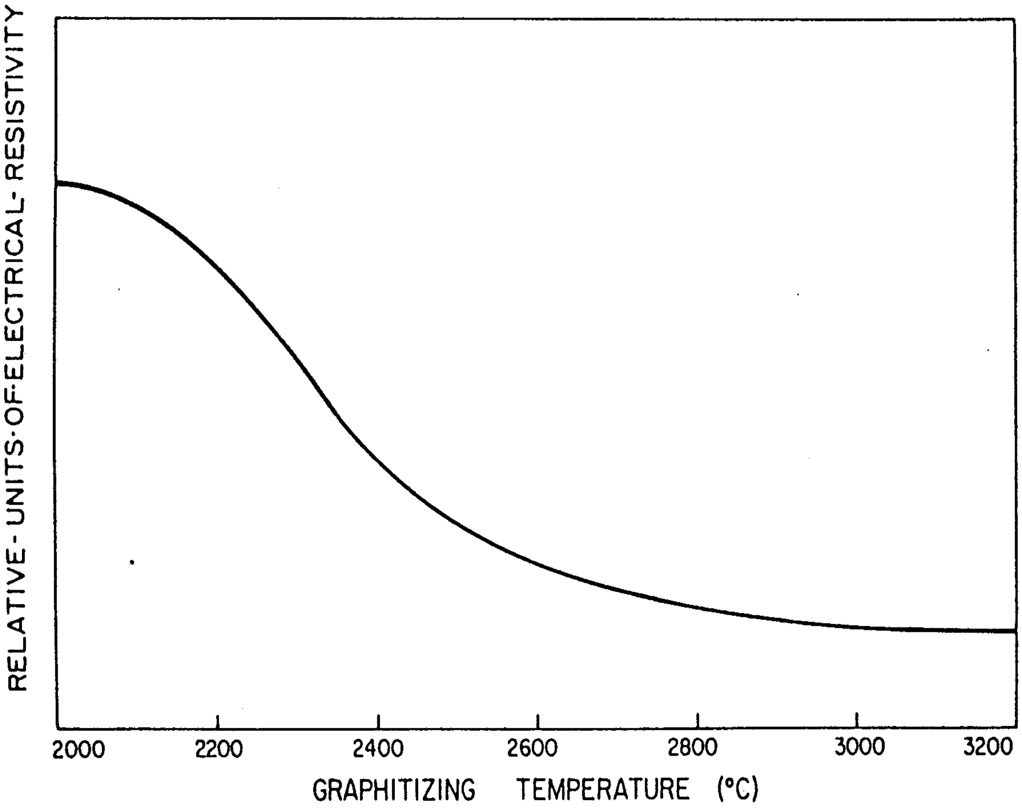
Property	Increase	Decrease
Resistivity		X
Apparent density		X
Strength		X
CTE		X
Porosity	X	
Weight		X
Modulus of elasticity		X
Thermal conductivity	X	

Typical Change in properties during graphitization



Mechanical properties versus graphitizing temperature

Typical Change in properties during graphitization



Electrical resistivity versus graphitizing temperatur

Typical expansion during graphitisation

Room temp. up to final baking temperature:	Apart from the thermal expansion no additional changes.
900 - 1200°C: (1173 - 1473°K)	As the calcination temperature of the filler component is surpassed, the incipient graphitic structure commences slowly.
Up to 1500°C - 2000°C: (1773 - 2273°K)	Hydrogen and sulphur from the binder are evolved (puffing) and an irreversible volume expansion occurs.
1800°C surpassed: (2073°K)	The graphitic structure proceeds more rapidly and increases beyond 2200°C.
Up to 2600°C: (2873°K)	A volume contraction takes place and crystallite growth predominates.
3000°C: (3273°K)	Thermal and electrical conductivity reach the optimum.

Development of crystallite alignment during graphitisation change by picture Harry Marsch

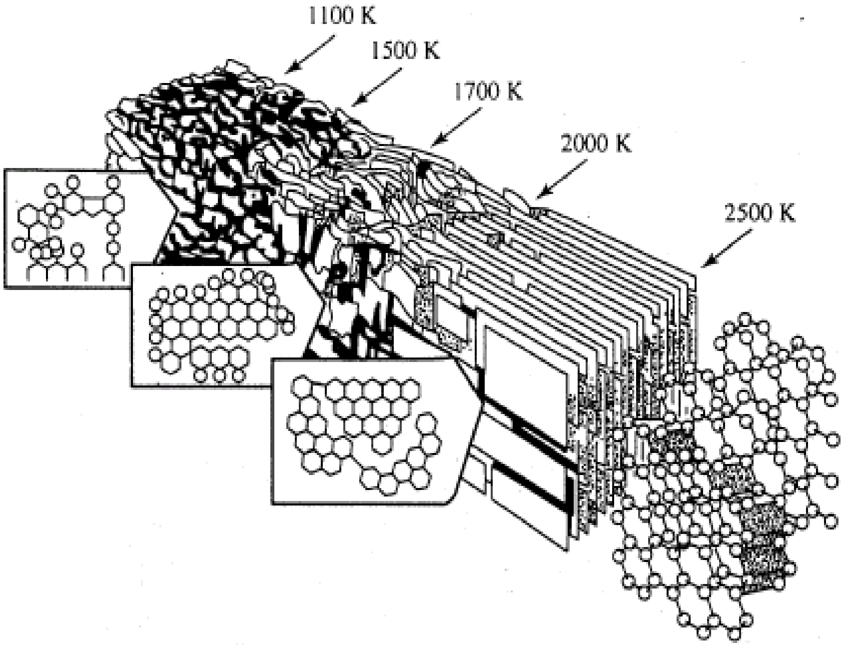


Figure 11.2.
Development of crystallite alignment during graphitization [4].

Heat treatment Graphitisation-Acheson

Acheson furnace

The stock is arranged in blocks within a horizontal bed, usually perpendicular to the axis of the furnace (click here for the picture of the Acheson furnace). The space between these segments is filled with a resistor material consisting of a coke/graphite granular mixture. The current is supplied to the load by two water-cooled head electrodes at the narrow sides of the furnace, which is thermally insulated by a mixture of coke, sand, carbon black and/or sawdust, thus protecting the material against oxidation. As the electrical resistance of the furnace decreases with an increasing degree of graphitisation, the power to the head electrodes is controlled and adjusted by transformers. Nowadays, nearly all graphitising furnaces are DC-operated since powerful rectifiers are available. For fine-grained material, an uncontrolled release of decomposition products from the charge does not cause problems, so that the normal maximum temperature of 2800°C can be reached within a few days. Depending on the size of the furnace and its operation mode, one working cycle including cooling lasts two to three weeks.

Comparison with Archeson furnace

Acheson furnace

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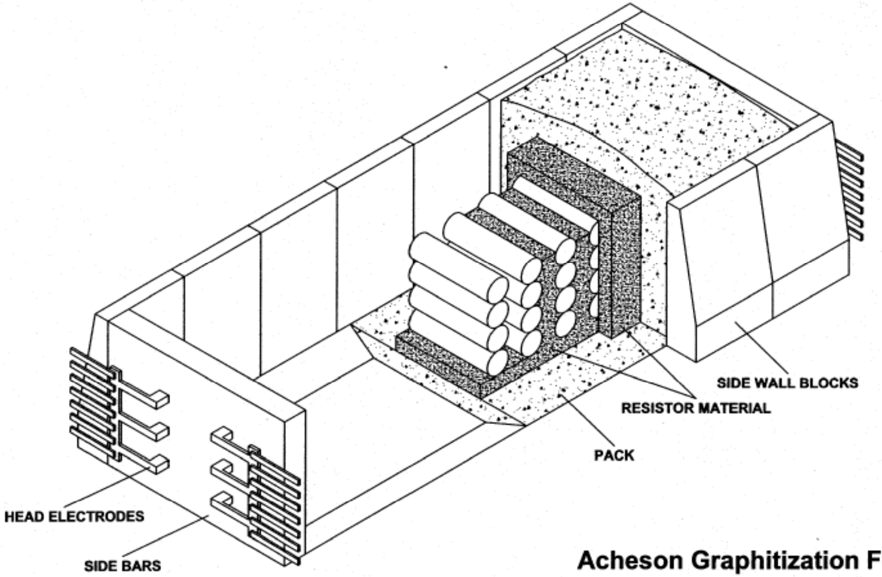


Acheson Graphitization Furnace

(BU CG EU)

Damm (GGIT) 29-VIII-2000 gph-f-q.dwg+grph2.pcp

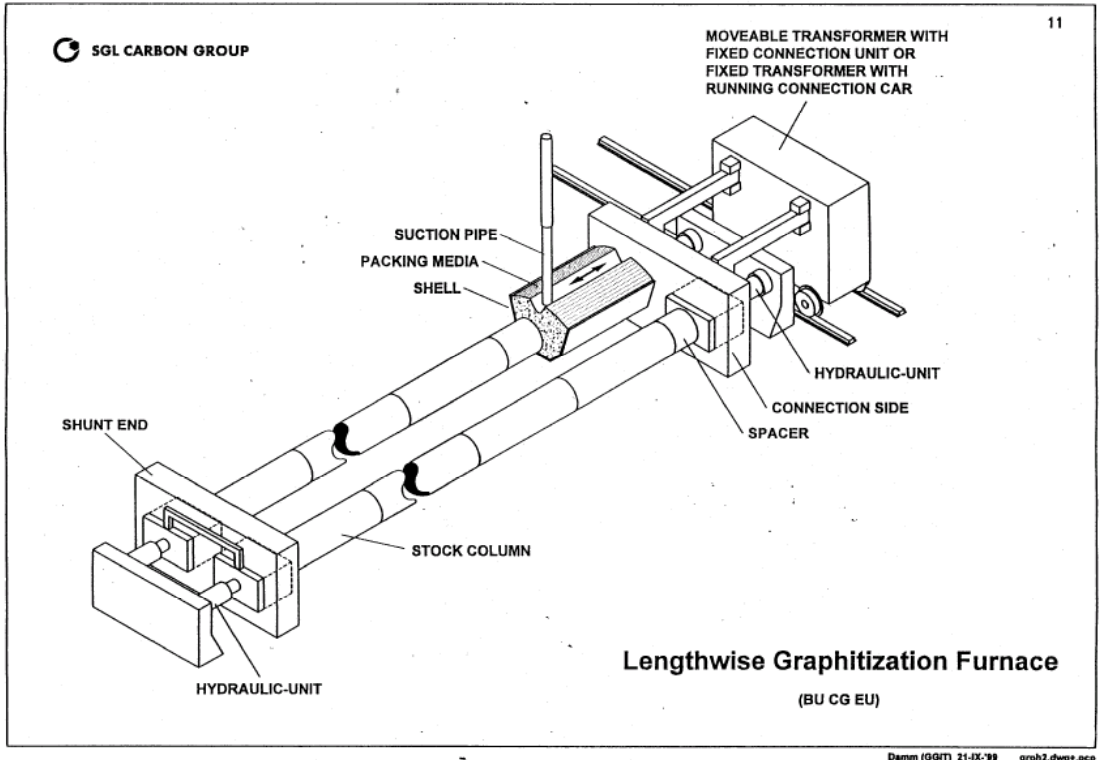
Heat treatment - Graphitisation

Castner furnace/longitudinal graphitisation

Lengthwise graphitisation (longitudinal array) was first described by Castner, and is characterised by the direct connection of the stock one to another in a row without a resistor material in between (click here for the picture of the Castner furnace). The artifacts are clamped between the head electrodes of the furnace and heated by passing the current directly through the load. The contact area of the material to be graphitised has to fit well and therefore requires plane-parallel machining and an adjustable clamping device in order to secure a constant, tight electrical contact for a low-contact resistance. The insulation against oxidation and high heat losses is the same as for Acheson furnaces. This graphitising method has the advantage of shorter heating periods, less power consumption and smaller furnace dimensions.

Comparison with Archeson furnace

LengthWiseGrapitisation (Castner) furnace



Lengthwise Graphitization Furnace

(BU CG EU)

LWG vs. Acheson

Advantages of the LWG over the Acheson furnace:

- Lower energy
- Reduced cycle time
- Better control of process for electrode

Production – Inductively heated

Inductively heated furnaces

Inductively heated furnaces are normally used for parts, which need to be graphitised with a very well controlled temperature profile. Indirectly heated furnaces consist of a horizontal or vertical graphite tube of rectangular or cylindrical cross-section. The outside of these tubes is insulated with carbon black surrounded by a carbon felt jacket. The material is passed through the furnace, either continuously or at intervals. It is protected from oxidation by using water-cooled seals at the ends of the furnace and by applying a stream of inert gas. The main advantage of such furnaces is very close temperature control.

Production - purification

Purification of Graphite

- The graphitising process is also accompanied by a purification of the material treated, normally reducing the content of impurities to considerably less than 1000 ppm. For many applications, this purity is insufficient, so that a thermal purification at higher temperatures up to 3100°C with longer residence times is carried out to reduce the impurities to a concentration of less than 200 ppm. If still lower ash values are required, a thermo-chemical purification is necessary.

Production - purification

Thermo-chemical purification

Even after graphitisation at around 3000°C most graphites contain small amounts of metallic impurities. If the ash values in the material have to be below 200 ppm, thermal purification is applied. By adding gaseous halogens or halogen compounds, all hetero-atoms forming stable carbides are transferred into volatile halogen compounds and thus removed. By means of this procedure, impurities may be lowered to less than 1 ppm.

Fabrication - machining

Machining graphite

Graphite can be machined wet or dry with ordinary machine tools but is normally machined dry. The different steps are dust extraction, cutting, turning, grinding, bonding and polishing. Click here for safety recommendations when machining graphite.

Fabrication - dust

Dust extraction

Individual extraction arrangements are essential on all machines when dry machining is carried out. Centralised extraction equipment is not worth installing except in large graphite machine shops. Where workshops are predominantly engaged in metal machining it is enough to install industrial vacuum cleaners on individual machines (vacuum 300mm head of water or air velocity of about 18 m/sec).

When machining carbon and graphite it is important to prevent ingress of dust into electrical motors and control panels.

Fabrication - cutting

Cutting

Cutting of graphite does not necessarily require specialist tools. However optimum results may be achieved using diamond cutting wheels.

Fabrication - drilling

Drilling

For drilling graphite, hard metal drills are used. To avoid chipping at the drilling exit the point angle should be 70-100° and the clearance angle 10-15°.

Fabrication - turning

Turning

Specialist machine tools for the turning of graphite are not absolutely necessary and a wide range of machines are in use, from wood turning lathes to CNC lathes. The machines normally have to be adapted to accommodate graphite machining, in particular protection of electrical equipment from dust.

Fabrication - roughening

Roughening

The surface of the graphite is made rough by silicon carbide wheels with a grain size of 20-46 µm and hardness F-K depending, on the hardness of the carbon material.

Fabrication - milling

Milling

Specialised milling machines are not required but optimum results may be obtained using hard metal or diamond tools.

Fabrication - finishing

Superfinishing

Depending on the hardness of the graphite material electro-corundum wheels with grain size 120-160 µm and hardness P-Z are used.

Fabrication - bonding

Bonding

It is possible to bond graphite; for this process all surfaces must be free of dust and grease. Bonding materials are polyesters, phenolic resins, epoxy resins and silicon resins. For high temperature use, ceramic bonds are available using aluminium oxide or zirconium oxide as a base.

Fabrication

Copy milling and form grinding

Preferred machining methods for the manufacture of Electric Discharge Machining (EDM) electrodes are milling and high-speed milling, form-grinding and EDM-cutting. Since EDM fine-grained graphite grades still have a volume of open pores of 10 to 15%, they can be impregnated with copper. Thus the advantages of the metal are combined with those of the graphite without impairing its excellent machinability. In spite of the large block dimensions available nowadays, a complicated graphite electrode sometimes cannot be manufactured in one piece. However, it is possible to bond several parts by means of commercially available one and two-component adhesives.

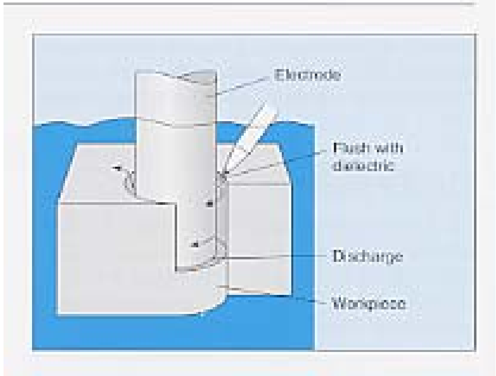
Fabrication - EDM

Electric Discharge Machining

Electric Discharge Machining is an electro-thermal erosion process for the machining of many electrically conductive materials, and it exploits the erosion effect of electric discharges between two electrodes. The tool is connected as an anode in an insulating liquid (dielectric liquid) and brought close to the work-piece cathode. DC-voltage induces an electric discharge. By this conversion of electrical into thermal energy, the cathode material is melted, evaporated, and eroded (figure). The fast and efficient manufacture of even the most complicated EDM-electrodes plays the decisive role for the economy of this method. Isostatically pressed fine-graphite grades are extremely cost effective electrode materials as they have, besides their electrical and thermal conductivity as fundamental requirements, also high mechanical strength, edge stability, surface quality and good machinability.

Fabrication

Figure of Electric Discharge Machining



Fabrication - finishing

Finishing and Surface Treatment

Due to its manufacture, a carbon artifact contains open pores, which may make up one quarter of its volume. By filling these pores, the density, strength and conductivity of the artifacts can be increased to predetermined levels. Closing the surface pores will also reduce oxidation. Impregnating agents are usually pitch, resins and metals, which are brought into the formed bodies by a vacuum/pressure impregnating cycle. Pitch-impregnated artifacts have to be rebaked in order to carbonize the pitch, whereas resin-impregnated parts are either thermally cured and/or carbonized. The rebaking step also causes new pores to form, so that at least one more impregnating operation is necessary if a high degree of gas or liquid-tightness is requested. Usually, completely gas or liquid-tight grades are manufactured by an impregnation with furan or phenolformaldehyde resins, which are subsequently thermally cured. This resin impregnation, however, reduces the temperature stability of such grades to a maximum of only 200°C or slightly above.

continue

Fabrication - finishing

Finishing and Surface Treatment

This limit may be increased by approximately 100 degrees by means of impregnating agents that have a higher thermal resistance, e.g. polytetraflu oroethylene waxes. Wax, grease, oil, and salts play an important role as impregnating agents for special applications - in particular for carbon brushes. Not only the physical properties of the grades but also their operating behaviour in electrical service can be improved. Upon pyrolysis of gaseous hydrocarbons, so-called pyrocarbon can be deposited in the pores or on the surface of the substrates so that the density, strength and corrosion resistance of the artifacts are also considerably increased. Oxidation resistance up to elevated temperatures of approximately 800°C may be reached by impregnation with borates or phosphates, whereas an efficient protection agains oxidation at higher temperatures may only be achieved by coating with silicides, borides, carbides or nitrides.

Fabrication
High grades surface finishing

- **Honing**

  Silicon carbide stones of grain size 69-99 um are used. In special cases for hard carbon it is also possible to use diamond coated honing strips depending on the required level of surface finish. Honing is done using the standard honing oils.

- **Lapping**

  This process uses lapping powder of aluminium oxide and silicon carbide in grain sizes 1 2-1 6 pm.

- **Polishing**

  It is essential to achieve a high degree of lapped finish before polishing is carried out. Diamond powder in grain sizes 6-10 pm is used. After machining it is essential to remove the media used (honing oil, lapping and polishing powder) from the work parts.

- **Ultrasonic dust removal**

  Where dust-free surfaces are required, ultrasonic dust removal can be carried out. The media used for this are water, distilled water or solvents.

Fabrication - surface

COATING

Surface properties of the material coated

When using pyrolytic graphite coatings following surface properties may be obtained or modified:

Electrical	resistivity
Optical	reflectivity
Mechanical	wear
	friction
	hardness
	adhesion
	toughness
Porosity	surface area
	pore size
	pore volume
Chemical	diffusion
	corrosion
	oxidation

Fabrication - coating

Coating Graphite

There are several coatings for graphite parts such as there are silicon carbide (SiC), pyrolytic carbon coating (PyC). The graphite properties vary depending on the coating.

Silicon carbide (SiC)

A pyrolytic carbon or graphite coating

Fabrication - coating

Silicon carbide (SiC)

Silicon carbide can be used as a coating for graphite parts. SiC coatings are deposited from gaseous silicon and carbon compounds at high temperatures (CVD process). The coefficient of thermal expansion of the graphite material must be matched to that of the SiC coating. The typical thickness of the SiC coating on graphite is 50-100 um. Edges of graphite parts should be radiused before coating. The coating renders the graphite with special properties.

Properties of SiC

- zero porosity (graphite parts can be sealed completely by appropriate thickness of coating)
- high hardness figure
- good thermal conductivity
- high oxidation resistance
- high purity

Fabrication - coating

A pyrolytic carbon or graphite coating

A pyrolytic carbon or graphite coating on a graphite substrate is produced at high temperature and pressure in a hydrocarbon atmosphere (e. g. methane or acetylene) using the CVD process.

Pyrolytic graphite production is based on a gaseous precursor. Pyrolytic graphite is an aggregate of graphite crystallites, which have dimensions (L_c) that may reach several hundred nm. It has a turbostratic structure, usually with many warped basal planes, lattice defects, and crystallite imperfections. Within the aggregate, the crystallites have various degrees of orientation. When they are essentially parallel to each other, the nature and the properties of the deposit closely match that of the ideal graphite crystal. The structure of a pyrolytic graphite deposit can be either columnar, laminar, or isotropic, depending on the deposition conditions such as temperature, pressure, and composition of the input gases. It is possible to obtain the desired structure by the proper control of these deposition parameters. The properties for columnar and laminar pyrolytic graphites differ from those of isotrophic.

Properties of pyrolytic graphite Application of pyrolytic graphite

Fabrication – properties PyC

Properties of PyC

- high density
- no porosity
- high anisotropy
- smooth surface

The anisotropic property comes from the growth of the pyrolytic carbon layer in parallel lattice planes. Edges of graphite parts should be radiused before coating. Parts should be purified before coating.

Fabrication - coating

Table: Properties of columnar and laminar pyrolytic graphites

Density (g/cm^3)	2.10 – 2.24
Flexural strength tested across grain (MPa)	80 – 170
Tensile strength tested in ab directions (with grain (MPa)	110
Young's modulus of elasticity (Gpa)	28 - 31
Thermal conductivity (W/m*K	
c direction	1 – 3
ab directions	190 - 390
Thermal expansion 0 – 100°C (x 10^{-6}/m*K)	
c direction	15 – 25
ab directions	-1 to 1
Electrical resistivity (μΩ*m)	
c direction	1000 – 3000
ab directions	4 – 5

Application

Application of pyrolytic graphite

High temperature containers

Boats and crucibles for liquid-phase epitaxy

Crucibles for molecular-beam epitaxy

Reaction vessels for the gas-phase epitaxy of III-V semiconductor materials such as gallium arsenide

Trays for silicon-wafer handling

Free-standing products

Propellant rocket nozzles

Resistance heating elements

Nuclear applications

Biomedical applications

Coatings for molded graphites

Coatings for fibres

Carbon-carbon infiltration

Fabrication - CVD

Chemical Vapour Deposition

CVD is a vapour phase process, which relies on the chemical reaction of a vapour near or on a heated surface to form a solid deposit and gaseous by-products. The process is very suitable to the deposition of carbon. It is used frequently in areas such as semiconductors and cutting tools. Special CVD processes are Chemical vapour infiltration, fluidized bed CVD and plasma CVD.

Fabrication

Chemical vapour infiltration

Chemical vapour infiltration (CVI) is a special CVD process in which the gaseous reactant infiltrates a porous material such as an inorganic open foam or a fibrous mat or weave. The deposition occurs on the fibre (or the foam), and the structure is gradually densified to form a composite. The process is used extensively in the production of carbon-carbon materials.

Fabrication

Fluidized bed CVD

Fluidized-bed CVD is a special technique, which is used primarily in coating particles such as nuclear fuel. A flowing gas imparts quasi-fluid properties to the particles. The fluidizing gas is usually methane, helium, or another non-reactive gas. Factors to consider to obtain proper fluidization are the density and size of the particles to be coated, and the velocity, density, and viscosity of the gases. The major applications of pyrolytic carbon deposited by fluidized bed are found in the production of biomedical components such as heart valves and in the coating of uranium carbide and thorium carbide nuclear-fuel

Fabrication

Plasma CVD

The deposition of graphite can also be obtained by plasma CVD, with the following characteristics:

- Gases: propylene-argon or methane-argon
- Plasma: radio frequency (RF) at 0.5 MHz
- Pressure: <1300 Pa
- Temperature: 300 – 500

In a plasma-activated reaction, the substrate temperature can be considerably lower than in thermal CVD. This allows the coating of thermally sensitive materials. The characteristics and properties of the coating are similar to those of coatings deposited at higher temperatures (>1000°C). Plasma activation is also used extensively in the deposition of polycrystalline diamond and diamond like carbon (DLC).