Carbon Production

Introduction:

As carbon does not melt under normal pressure, carbon bodies can be manufactured the same way as ceramics, from mouldable mixes of carbonaceous solids and binding agents by the subsequent carbonization of the shaped articles. During the carbonizing process, the binder is converted into a solid coke residue, while the volatile matter (including degradation products) is evaporated. The conductivity of such material is considerably lower than that of graphitized grades, but is sufficient for many applications.

The largest market for this type of carbon product is for anodes for aluminium production. There is a large variety of other applications.

Carbon Production

- **Mixing**
- **Moulding and die-moulding**
- **Extrusion**
- **Baking and Furnaces**
- **Baking furnaces**
  * **Ring furnace**
  * **Single-chamber furnace**

Carbon Production & Machining

Production

- Milling

  As most solid raw materials do not have a grain size suited to direct processing, they have to be broken down to the desired particle size, sometimes in several steps using different equipment.

  Crushers and impact mills are used for producing grain sizes between 25 mm and 0.1 mm (0.04 and 0.004 in.).

  For finer milling to particle sizes less than 0.1 mm, pin, pendulum, tube, ball, impact and jet mills are used. In addition to the hardness of the material to be milled, its required grain size and particle size distribution play an important role in selection of the appropriate mill.

Production

Mixing

Mixers are used to homogenize and uniformly mix the solid compounds with the binding agent. In this process, the solids are placed into the mixer; and, during homogenizing heated by gas burners, steam or electric energy. In some special cases the solids are blended and homogenized in a separate dry mixer. The binder is added to the filler in liquid or solid form in an amount appropriate for the moulding procedure selected. Mixes with identical grain size distributions have a higher binder requirement in the case of extrusion than those, which will be die-moulded or iso-statically pressed. Predominantly low-speed sigma-blade mixers or paddle mixers are used. The mixer capacity may vary between several hundred to 2000 litres. The final mixing temperature is 120 to 200°C for a period of 20 to 120 minutes. The hot mixes are cooled to room temperature and then milled to the grain size requested for the shaping procedure. For mixes to be die-moulded, a technique called "evaporative mixing" is used to obtain a high level of density and strength, by vaporizing for up to several hours a proportion of the lower boiling fractions of the binder at the final mixing temperature.

Production

- **Forming**

For forming the green mixes, normally four methods are used, which are extrusion (continuous process), die-moulding (discontinuous process), isostatic pressing (discontinuous process) and vibrating (discontinuous process).

The material properties and potential applications are greatly influenced by proper selection of the forming process. The mix consists of predominantly anisotropic particles, which obtain a distinct orientation according to the respective moulding process. The orientation is parallel to the forming direction in the case of extrusion, and perpendicular to it with die-moulding. Therefore, the formed artifacts show a varying anisotropy of their properties according to their grain configuration, thus making them unsuitable for certain applications.

Production

Die-moulding

Die-moulding is a discontinuous forming process in which the mould is filled with the material to be moulded and is subsequently compacted by a ram to the desired height of the artifact. Very often one works simultaneously with upper and lower rams, since an ejection device is needed anyway in order to release the shape from the mould. Die-moulding generates a much less distinctive anisotropy than extrusion.

Die-moulding is mostly used for small-dimensioned fine-grained carbon and graphite parts, and may be automated in the case of large quantities of the same shape. When the shrinkage in volume, due to subsequent thermal treatment, is properly taken into account, many parts may be manufactured in one step - either pressed to final size or at least to near net shape - so that a subsequent machining process may be partially or even completely omitted.

Die-moulding calls for very sophisticated tooling when more complicated parts have to be produced. Isostatic pressing is reserved for the manufacture of large-dimensioned isotropic artifacts, e.g. with cross-sections of 1000x1500 mm, and also requires high expenditure for producing the flexible moulds.

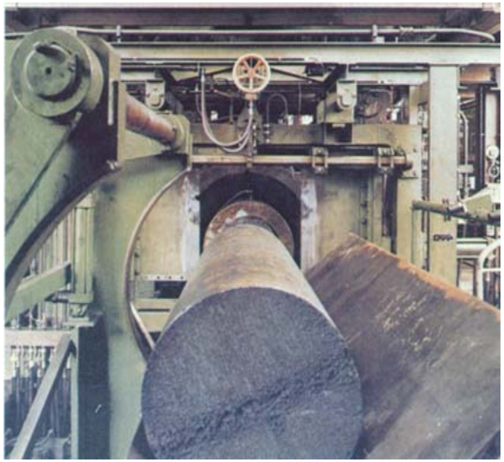
Production

Extrusion

Extrusion is a continuous forming process in which the mix is filled into a large storage chamber of the press (mud chamber), compacted by means of a piston in the direction of the die exit and pressed out as a practically endless shape.

When the pressing chamber is empty, the piston is retracted, and the storage section is filled again to repeat the pressing cycle.

In order to overcome high friction forces, the inner diameter of theremovable die is reduced step by step. The die exit shape will differ according to the desired cross-section or profile of the extruded material.

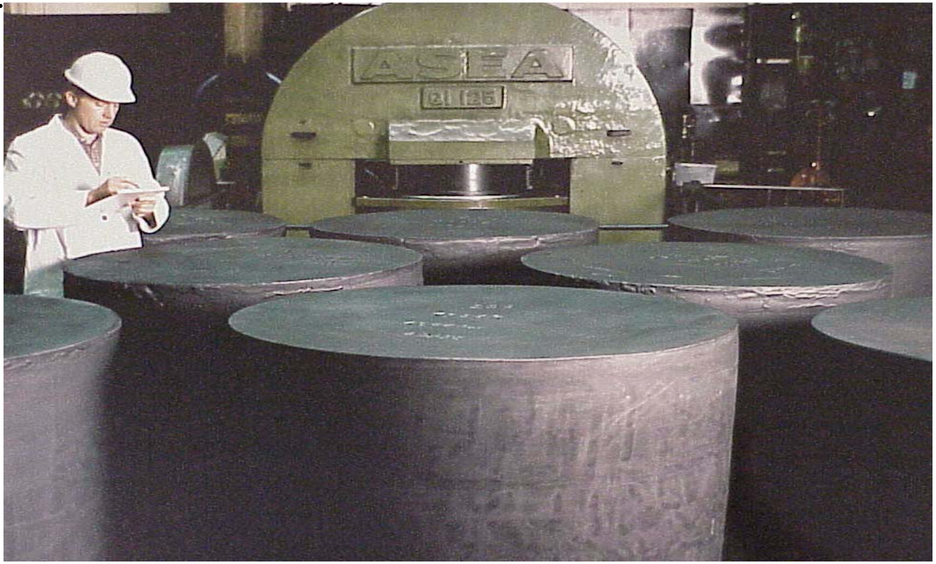


Extrusion generates a much more distinctive anisotropy than die-moulding. By means of the continuous extrusion process, cylindrical, rectangular/square, or even more complicated cross-sections of several square millimetres up to several thousand square centimetres are produced which are cut to the desired length for further processing.

Production of Carbon

Isostatic pressing

Isostatic pressing is also a discontinuous forming procedure, having the advantage that the compacting force is applied uniformly from all directions. This is indispensable for the manufacture of isotropic large-dimensioned bodies. An elastic mould is filled with the material to be moulded, inserted into the liquid within a pressure vessel and compacted by applying high pressure to produce the desired shape. Isostatic pressing, even with highly anisotropic particles leads to nearly isotropic artifacts due to the uniform exertion of the pressing forces onto the flexible moulds.



Production

Vibration

Vibrating is a discontinuous forming process for large dimension products. A mould is filled with the milled powder and a heavy metal plate is put on top of the powder. Then the material is compacted by vibrating the mould for a certain period of time. The formed bodies show a higher degree of isotropy compared to extruded or die-moulded material.

Production

Baking

Carbon is oxidised at elevated temperatures. Therefore, the presence of air or other oxidising agents has to be excluded. During the baking process, the binder bridges between the solid filler particles are carbonised, i.e. converted into solid carbon, which produces the required strength of the artifact. This process may be broken down into four steps:

1. heat transfer from the outside into the interior
2. Pyrolysis/carbonization of the binding agent
3. transport of volatile pyrolysis products to the outside
4. cooling to room temperature

purpose furnaces

Purpose of baking

The purpose of the baking process is to

- change the binder pitch chemically by heating,
- converting it into a solid carbon mass
- which forms permanent carbon bonds between the coke particles.
- Thus a permanent solid rigid body is formed.

detail

Purpose of baking in detail

- The purpose of baking is to cement or bond the coke particles together by converting the binder pitch to a solid carbon residue.
- The coke particles of the green stock are held by stickiness of the binder pitch in its solid state at room temperature.

  However, if the binder pitch is heated to its softening point, the pitch will melt and the green product will deform or fall apart.
- Thus, the baking process is used to change the binder pitch chemically by heating, converting it into a solid carbon mass which forms a permanent carbon bond between the coke particles.
- Thus a permanent solid rigid body is formed.

Production

Liquid-phase pyrolysis, is a controlled thermal treatment of molten condensed aromatic compounds under the exclusion of oxygen in the temperature range between 200 and 600°C. The carbonising process is aimed to maximise coke yield, which is accompanied by a low formation of volatile decomposition products. The rate of the temperature increase in the furnace and within the artifact plays a decisive role as a rapid pyrolysis leads to an increased generation of volatile pyrolysis products, and too strong a shrinkage of the shaped bodies results in the formation of cracks and ultimate destruction of the artifacts. During the pyrolysis phase, between 250 and 550°C, the temperature increase should be approximately 0.5 to 5 degrees per hour, although it can be considerably higher up to the final temperature which, depending on the application or further processing, may be from 650 to 1300°C. The artifacts are set into the chambers of a furnace and embedded in packing media, e.g. coke granules with or without sand, in order to ensure uniform heat transport and distribution, to maintain the dimensional stability of the shapes during the plastic phase of the binder, and to protect the carbon from oxidation.

The load is large and has poor thermal conductivity, slow baking rates are necessary to keep temperature differences at a minimum. Baking cycles from 20 to 72 days, depending on the furnace size and product mix are not unusual.

Baking Furnaces

Ring furnace

Single-chamber furnace

Baking Furnaces

Furnaces

Baking furnaces are usually oil or gas-fired kilns, single-chamber furnaces or tunnel kilns. Small-dimensioned parts are also baked in electrically heated muffle, pit or push-rod furnaces. In ring furnaces and single chamber furnaces, it is possible to place the stock into steel containers (saggers), embed them in the packing material, and arrange these saggers in the chamber instead of placing pieces directly into the brick boxes of the furnace chamber. This handling is preferred in the case of shapes of different dimensions, as it allows a more advantageous usage of space. Also the loading and unloading procedures can be automated.

Baking Furnaces

Ring furnace

A ring furnace is a kiln with 20 or more chambers interconnected forming a ring and having the advantage of the most efficient utilisation of the heating energy as the chamber just being fired preheats the other unheated chambers with gaseous pyrolysis products from the binder. At the same time, the fresh air for the burners is passed over the already fired chambers, thus cooling them down and warming itself by heat exchange. One cycle for one chamber with a final temperature of 1000°C and an average heating rate of two degrees per hour takes three weeks. The burner device is then transferred to the adjacent chamber, so that a kiln of this type can be operated continuously for several years. The major disadvantage of a ring furnace is limited temperature control. Due to the coupling of the chambers, temperature changes have a marked influence on the entire furnace.

loading a ring furnace

Loading - Ring Furnace

- Furnace Cell Bottoms Are Covered With A Sheet of Aluminum coated Paper to Prevent Pitch and Packing Media From Sticking
- Furnace Cell Bottoms Are Covered With A Specified Amount of Packing Media
- Stock Is Loaded Vertically In One or Two Layers, In Single or Multiple Rows
- Spacings Are Specified For: Stock-To-End, Stock-To-Side, and Stock-To-Stock Distances
- A Minimum of 250mm of Top is Required
- A Layer of Refractory Bricks Are Placed on Top of Media to Reduce Oxidation And Blowing Into Flue Ports

Baking Furnaces

Single-chamber furnace

Pit furnaces may be rate-controlled with variable temperature programs, but they are not that economic in utilizing the heat energy. Therefore, they are mostly used for smaller lot-sizes requiring variable heating programs.

A car-bottom baking furnace is a special type of a single-chamber furnace. Here, a flat-bed car with containers is removed from the furnace after baking and a newly prepared car is immediately brought in. Possible automation also offers a considerable advantage. Electrically heated furnaces for small-dimensioned parts are operated in the same way. Push-rod and conveying-belt furnaces, which are used for the manufacture of parts pressed to size, or to near net shape, are operated in an inert atmosphere. Therefore, the embedding of the parts in the packing media may be omitted.

Fabrication - machining

Machining baked carbon

Baked carbon can be machined wet or dry with ordinary machine tools. Changes between wet and dry working on the same machine are best avoided. The different steps are dust extraction, cutting, turning, milling, lapping and polishing.

Baked carbon is very hard and therefore it is preferably machined with diamond faced tools.

Fabrication – dust extraction

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).

Fabrication - cutting

Cutting

Carbon is cut with bronze-matrix diamond cutting wheels, grain size 200-300 microns, at a peripheral speed of 50-60 m/sec. The cutting speed is 300-600 m/min.

Fabrication - drilling

Drilling

For drilling carbon, hard metal or diamond coated 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

The work piece is best held in a spring collet or with an expanding ring and the clamping pressure spread over as large an area as possible in view of the ceramic nature of graphite. Where close tolerances are needed it is advisable to use diamond tools. By applying radii or chamfers to the edges of the tools chipping of the work piece is reduced.

Fabrication - milling

Milling

This is carried out with hard metal or diamond tools. The clearance angle should not be less than 10°. Cutting speed can be increased up to 50% by using diamond tools.

Fabrication - finishing

Superfinishing

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

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 re-baked in order to carbonize the pitch, whereas resin-impregnated parts are either thermally cured and/or carbonized. The re-baking 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.

Fabrication - finishing

- **Finishing and Surface Treatment (continued)**

  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 against oxidation at higher temperatures may only be achieved by coating with silicides, borides, carbides or nitrides.

Fabrication – high grade surface finish

- **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

Properties of isotropic pyrolytic carbon

- Good hardness: easy to polish, material can have high gloss, good wear resistance
- Mechanical property: reasonable structural material
- Good gas permeability

<u>Table: properties of isotrophic Pyrolytic Carbon at 25°C</u>

Density (g/cm^3)	2.1
Vickers Diamond Pyramid Hardness (kg/mm^2)	240 – 370
Flexural strength (MPa)	350
Young's modulus (Gpa)	28
Strain to failure (%)	1,2

Application

Application of pyrolytic carbon

- 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 moulded graphites
- ➢ Coatings for fibres
- ➢ Carbon-carbon infiltration

Properties pyrolytic carbon

Table: Properties of columnar and laminar pyrolytic carbon

Density (g/cm^3)	2.15 – 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 ab directions	 1 – 3 190 - 390
Thermal expansion 0 – 100°C (x 10^{-6}/m*K) c direction ab directions	 15 – 25 -1 to 1
Electrical resistivity (μΩ*m) c direction ab directions	 1000 – 3000 4 – 5