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(57) Abrégé/Abstract:
The present invention relates to a carbon body which is produced by burning a mixture which contains at least coke. According to the invention, the coke is a coke of low graphitizability. In addition, the present invention relates to a method for producing a carbon body, which method comprises the steps mixing anthracite, graphite and/or coke or mixtures thereof, at least one binder from the group of petroleum- or coal-based binders, and also synthetic resin-based binders and any mixtures of said binders and optional additives, shaping the mixture to a predetermined shape, burning the shaped mixture and optionally graphitizing the burnt shaped body, wherein the coke is a coke of low graphitizability.

Abstract

The present invention relates to a carbon body which is produced by burning a mixture which contains at least coke. According to the invention, the coke is a coke of low graphitizability. In addition, the present invention relates to a method for producing a carbon body, which method comprises the steps mixing anthracite, graphite and/or coke or mixtures thereof, at least one binder from the group of petroleum- or coal-based binders, and also synthetic resin-based binders and any mixtures of said binders and optional additives, shaping the mixture to a predetermined shape, burning the shaped mixture and optionally graphitizing the burnt shaped body, wherein the coke is a coke of low graphitizability.

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CARBON BODY, METHOD FOR PRODUCING A CARBON BODY AND USE THEREOF

The present invention relates to a carbon body, a method for producing a carbon body and use thereof.

Carbon bodies are used as components in the chemical industry, where they are often exposed to aggressive chemicals and high temperatures. The requirements of these components are high and they have a limited lifetime.

Cathodes made of nongraphitic carbon and graphite are used as the bottom lining of aluminum electrolysis cells, for example. These materials combine a very good electrical conductivity with a high thermal stability and chemical resistance. Graphitized cathodes in particular are suitable for modern high-amperage cells because of their excellent electrical conductivity. However, these cells are subject to severe erosion during operation as anthracite-based cathodes, for example. The erosion is concentrated at the ends of the cathodes, where a high current density prevails, resulting in the development of a W-shaped profile. Mechanical influences play a not insignificant role because the molten aluminum layer on the cathode surface is constantly in movement due to the high magnetic fields. Furthermore, chemical attacks occur due to the components of the electrolysis bath. Both types of erosion limit the lifetime of the cathode blocks and thus of the electrolysis cell.

A cathode in which this problem is to be avoided is described in FR 2,821,365. This cathode comprises a carbon product that is reactive with sodium even after a treatment at a temperature above 2400°C. The sodium comes from cryolite, which is typically added to the electrolysis bath.

Blast furnace bricks are also manufactured from monographitic carbon or graphite. The erosion of blast furnace bricks preferentially in the tap hole area of the blast furnace is a technical problem with blast furnaces for iron production. Here in particular the molten crude iron excessively attacks the graphite and carbon lining both chemically and mechanically.

There is thus the problem that the carbon body is attacked by chemical and mechanical erosion, which therefore shortens its lifetime.

The present invention relates to a carbon body which has a long lifetime.

In one product aspect, the invention relates to a carbon body that is produced by burning a mixture containing at least coke, wherein the coke has a degree of graphitization according to Maire and Mehring of 0.50 or less after a thermal treatment of the coke at 2800°C, calculated from the average layer spacing c/2, and wherein the grain of the coke is greater than 0.5 mm.

In one process aspect, the invention relates to a method for producing a carbon body comprising: (a) mixing: (i) coke with anthracite, graphite or a mixture thereof, (ii) at least one binder selected from the group consisting of a petroleum-based binder, a carbon-based binder, a synthetic resin-based binder and a mixture thereof, and (iii) optionally, an additive; (b) shaping the mixture from step (a) to a predetermined shape; and

(c) burning the shaped mixture from step (b) and, optionally, graphitizing the resultant burned molded body, wherein the coke has a degree of graphitization according to Maire and Mehring of 0.50 or less after a thermal treatment of the coke at 2800°C, calculated from the average layer spacing c/2, and wherein the coke has a grain of greater than 0.5 mm.

According to the invention, a carbon body produced by burning a mixture that contains at least coke is made available, the coke being a coke with a low graphitizability.

A coke with a low graphatizability has a high hardness and abrasion resistance even after being exposed to a high temperature in the production process, which is up to 3000°C, for example. Due to the addition of coke with low graphitizability, the abrasion resistance of the surface of the carbon body is increased in comparison with traditional carbon bodies without the addition of the poorly graphitizable coke according to the invention. Coke with a low graphitizability acts in particular as an agent for producing a high abrasion resistance.

The coke with a low graphitizability preferably produces a higher bulk density of the carbon body in comparison with traditional carbon bodies.

The coke is preferably a coke with a spherical morphology. Due to its approximately spherical geometry, the coke increases the flowability of the mass in shaping the carbon body. The carbon body therefore advantageously has a higher bulk density than traditional carbon bodies. The carbon body therefore preferably also has a high wear resistance.

In addition to the coke, which has a low graphitizability according to the invention, the carbon body is preferably produced using anthracite, graphite and/or traditional coke, for example, petroleum coke or coal tar pitch coke, at least one binder, for example, from the group of petroleum-based or carbon-based binders such as tar, petroleum pitch, coal tar pitch, bitumen or a phenolic resin or furan resin and optional additives such as carbon fibers. The starting materials listed above may have different grain sizes. Recipes comprising the aforementioned starting materials for traditional carbon bodies, for example, a cathode block or a blast furnace are known. With carbon bodies that traditionally contain petroleum coke and/or coal tar pitch coke, preferably at least some of the petroleum coke and/or coal tar pitch coke is replaced by the coke with a low graphitizability.

In a preferred embodiment, the degree of graphitization according to Maire and Mehring is max. 0.5 or less after a thermal treatment of the poorly graphitizable coke at 2800°C, calculated from the average layer spacing c/2. During graphitization of the carbon body at a temperature up to 3000°C, the coke forms very little or no graphite structure and therefore retains its abrasion resistance and its high hardness.

In another preferred embodiment, the grain of the coke with a low graphitizability is greater than 0.2 mm, preferably greater than 0.5 mm. If the carbon body is to have a predetermined conductivity, the coke with a low graphitizability will be present in the carbon body in an amount of at most 25% by weight, based on the dry mixture. More preferably the coke is present in the carbon body in an amount of 10% to 20% by weight, based on the dry mixture.

Because of its spherical morphology, the coke with a low graphitizability is a molding aid with which a higher bulk density of the carbon body can be achieved in comparison with a traditional carbon body. In a preferred embodiment, the coke has a spherical to slightly ellipsoidal shape. Furthermore, it preferably has an onion skin structure which is consistent with its low graphitizability. In the sense of the present invention, the term "onion skin structure" denotes a multilayer structure comprising and inner layer with a spherical to ellipsoidal shape, which is covered completely or partially by at least one intermediate layer and one outer layer. The agent for creating a high bulk density and a high abrasion resistance is especially preferably a coke with a low graphitizability, a high hardness and a spherical structure composed like an onion skin.

The coke with a spherical to ellipsoidal shape preferably has a length/diameter ratio of 1 to 10, preferably 1 to 5, more preferably 1 to 3. The more the shape of the coke approximates a spherical structure, the better is the flowability of the mass and the better are the mechanical properties of the carbon body.

The coke used according to the invention is especially preferably hard and highly isotropic, difficultly graphitizable to nongraphitizable and has a low porosity and a low specific surface area, for example, in the range of 10 to 40 m^2/g, more preferably 20 to 30 m^2/g. However, the average layer spacing d_{002} of the coke, which can be determined by x-ray diffraction, is preferably 0.340 to 0.344 nm (this corresponds to a degree of graphitization of 0.0 to 0.5 according to Maire and Mehring) is no less than 0.339 nm after a thermal treatment at 2800°C. The apparent stacking height L_c is preferably less than 20 nm after a thermal treatment at 2800°C.

A specific representative of this coke with a low graphitizability is a coke obtained as a byproduct in the production of unsaturated hydrocarbons, in particular acetylene. The coke with a low graphitizability used according to the invention can be obtained in particular from crude oil fractions or steam cracking residues, which are used in quenching reaction gas in the synthesis of unsaturated hydrocarbons (acetylene), wherein the quenching oil/carbon black mixture is sent to a coker, which is heated to approximately 500°C. Volatile components of the quenching oil evaporated in the coker, from the bottom of which the coke can be removed. A fine-grained onion-skin coke, which has a high purity in addition to having the properties described above and has little to no ash and mineral content, is obtained in this way.

The coke preferably has a carbon content of at least 96% by weight and an ash content of at most 0.05% by weight, preferably at most 0.01% by weight.

A method for producing acetylene in which such a coke is obtained as a byproduct is described in DE 29 47 005 A1, for example. In this process, the coke with a low graphitizability as described above is produced from the quenching oil. To form the body according to the invention, petroleum coke in particular is at least partially replaced by the coke with a low graphitizability according to the invention in a traditional composition of the carbon body comprising petroleum coke.

The coke with a low graphitizability especially has a high purity and contains little to no ash and mineral content. However, the coke with a low graphitizability may also contain ash and minerals and may be less pure. The purity of the coke depends on the purity of the quenching oil used. Coke is usually a solid with a high carbon content and in the nongraphitic state and is produced by pyrolysis of organic material which has passed through a liquid or liquid crystalline state at least partially during the carbonization process. Presumably the carbon black particles prevent the development of an undisturbed liquid phase (mesophase) and supply a coke with a high hardness and poor graphitizability. Therefore, coke obtained from the gas quenching process can be graphitized only slightly by thermal treatment at temperatures above 2200°C. After a heat treatment at 2800°C, the average layer spacing c/2, as determined from the x-ray diffraction interference d_{002}, is 0.34 nm or more, and the crystallite size in the c direction L_c is less than 20 nm and the crystallite size La_{110} is less than 50 nm, preferably less than 40 nm. The coke used according to the invention especially preferably has a high hardness and a poor graphitizability, and the average layer spacing c/2 is greater than or equal to 0.34 nm after a thermal treatment at 2800°C.

As a rule, coke produced in this way is obtained in spherical particles of a few micrometers to a few millimeters. The coke with a low graphitizability used according to the invention preferably has grains larger than 0.2 mm, preferably greater than 0.5 mm. The preferred grain can be determined by screening and then suitable fractionation of the coke, for example. In a preferred embodiment, the coke with a spherical morphology has a BET surface area of 20 to 40 m^2/g. It has a very low porosity.

The coke with a structure like an onion skin may also have at least one extra substance in its structure. One example of this is the incorporation of carbon black particles such as those necessarily formed in acetylene synthesis.

In addition or as an alternative to the coke derived from the production of acetylene, coke from the fluid coking/flexicoking process (Exxon Mobil) may also be used according to the present invention as a coke with a low graphitizability. A coke obtainable from the fluid coking process also has a low graphitizability. Furthermore, it also has a spherical to ellipsoidal shape and is constructed by the onion skin principle. In comparison with the coke described above, which is obtained as a byproduct in the production of acetylene, this has a higher ash content. The x-ray structural data given above also applies to this coke.

In addition or as an alternative, a so-called shot coke (translated into German approximately as "scrap coke") from the "delayed coking process" can also be used in the sense of the present invention as coke with a spherical morphology. The limits of the x-ray structural data given above are to be modified in this case because of the somewhat better graphitizability. After a temperature treatment at 2800°C, the average layer spacing should be greater than 0.338 nm and the crystallite size in the c direction should be less than 30 nm. The abrasion resistance of the graphitized carbon body does not entirely achieve that of the coke variants described above. However, improved flowability of the mass is also obtained because of the spherical morphology of this shot coke and a carbon body of a high bulk density is achieved.

The carbon body is preferably a cathode block. In the case of cathode blocks, a distinction is made between an amorphous cathode block, a graphitized cathode block and a graphitic cathode block, depending on the raw material used and/or the production process. In a preferred embodiment, the carbon body is a graphitized cathode block. The carbon body is suitable as a cathode block because of its high abrasion resistance, hardness and conductivity.

In an alternative embodiment, the carbon body is preferably a graphitized blast furnace brick. The carbon body according to the invention can handle the thermal and mechanical loads of a blast furnace brick, in particular a blast furnace brick, which serves as the lining of a blast furnace for iron production. Molten iron in the blast furnace hardly penetrates into such bricks, so there is only minor wear on the bricks.

The method according to the invention for producing a carbon body includes the steps of mixing anthracite, graphite or traditional coke, for example, petroleum coke or coal tar pitch coke or mixtures thereof, at least one petroleum or coal-based binder and optionally at least one synthetic resin-based binder and optionally any mixtures of the aforementioned binders as well as optionally additional additives and at least one agent for creating a high bulk density, wherein the agent for creating a high bulk density is coke with a spherical morphology, then the mixture is shaped to form the predetermined shape, the shaped mixture is burned and then the burned mixture is optionally graphitized.

In the method according to the invention, at least one binder from the group of petroleum- or coal-based binders such as tar, pitch, bitumen or a phenolic resin or a furan resin is used.

The additives may be carbon nanofibers or carbon fibers, for example.

In the method according to the invention, the starting materials that are used to produce the carbon body are used in the respective desired grain(s). A starting material may optionally be screened prior to use. All the predetermined starting materials are mixed together, optionally under the influence of temperature and optionally kneaded. Then the resulting mixture is shaped and compacted. The shaping and compacting may be performed, for example, by extrusion, pressing or vibration molding, i.e., shaking in vacuo. Then the shaped body is fired. Next the carbon body may optionally be subjected to graphitization. Then the carbon body may be processed to yield the desired dimensions of its final shape.

The burning temperature in the embodiment without a subsequent graphitization surface is preferably 1100°C to 1500°C. If the carbon body is subjected to a graphitization, the burning temperature is preferably in the range of 700°C to 1100°C and the temperature in graphitization is in the range of 2000°C to 3000°C. The carbon body may be impregnated and burned again, before or after graphitization. Graphitization is preferably performed according to the Acheson graphitization process, more preferably according to the Length Wise Graphitization (LWG) process (Castner process).

In the method according to the invention, the coke with a low graphitizability used in this process is obtained from a quenching oil, which is used in quenching the reaction gas in the synthesis of unsaturated hydrocarbons, in particular acetylene (so-called acetylene coke). The coke preferably has a carbon content of at least 96% by weight and an ash content of at most 0.05% by weight, preferably at most 0.01% by weight. Spheroidal coke from the fluid/flexicoking process is an alternative to a coke from acetylene synthesis. Another alternative to a coke acetylene synthesis is shot coke from the delayed coking process. The two types of coke mentioned first are poorly graphitizable hard coke for which the x-ray structural data given above are applicable.

The coke with a low graphitizability, which is obtained in the production of acetylene as a byproduct, can be used in the method according to the invention in the form in which it is obtained from the process described above as disclosed in DE 29 47 005 A1. As an alternative, the coke may be thermally pretreated before being used in the method according to the invention. The thermal pretreatment comprises calcination, i.e., a heat treatment of the coke at a temperature in the range between 700°C and 1600°C, preferably 1000°C to 1500°C, more preferably 1100°C to 1300°C, optionally under a reducing atmosphere. Such a treatment leads in particular to evaporation of water, volatile flammable substances such as hydrocarbons, e.g., methane, carbon monoxide and/or hydrogen.

In a preferred embodiment, the coke with a spherical morphology and with a degree of graphitization according to Maire and Mehring after a thermal treatment of the coke at 2800°C, calculated from the average layer spacing c/2 of 0.5 or less, is used in the method according to the inventtion. The coke with a spherical morphology and a low graphitizability is an agent for creating a high bulk density and a high abrasion resistance.

The quantity of coke used with a spherical morphology is preferably at most 25% by weight, more preferably 10% to 20% by weight, based on the dry mixture. The coke with a spherical morphology with a grain larger than 0.2 mm, more preferably larger than 0.5 mm is preferably used.

The carbon body according to the invention can be used in a wide range. In particular because of its high bulk density, high abrasion resistance, high wear resistance, chemical inertia and high thermal stability, it is used as a component in machinery, chemical equipment or heat exchangers in the field of process technology, for example. In addition, because of its properties described above, the carbon body according to the invention is used as an electrode or lining of components in the production of substances which are manufactured under relatively aggressive conditions such as exposure to aggressive chemicals or high temperatures.

In a preferred embodiment, the carbon body according to the invention is used at a cathode block in an electrolysis cell for producing aluminum. By replacing a part of the traditional petroleum or coal tar pitch coke in traditional cathode block recipes with the special almost spherical hard coke which has a low graphitizability, a cathode block with a higher bulk density in comparison with traditional cathode block is obtained. Furthermore, the abrasion resistance of the cathode block surface is increased in comparison with that of traditional cathode block surfaces. Due to the higher bulk density and greater abrasion resistance, such a cathode is readily capable of withstanding corrosion during electrolysis to produce aluminum due to chemical stresses and in particular mechanical stresses.

Alternatively, the carbon body is preferably used as a blast furnace brick in a blast furnace for iron production. Because of the higher bulk density and higher abrasion resistance in comparison with traditional blast furnace bricks, the carbon body according to the invention as a blast furnace brick can withstand the mechanical stresses and thermal wear. The carbon body according to the invention is suitable in particular for use in the tap hole area of a blast furnace for iron production.

In another preferred embodiment, the carbon body according to the invention is used as an electrode in carbothermal reduction processes. For example, the carbon body according to the invention is used in carbothermal production of silicon in which silicon dioxide is reduced to silicon.

In addition, the carbon body according to the invention is preferably used as an electrode in electrothermal reduction processes or as a lining for a glass furnace, for example, for producing aluminum, titanium, silicon, iron, iron alloys, phosphorus, glass or cement and also as a shaping tool and/or as a lining for melting and holding crucibles as well as spouts and runout channels in the aforementioned regions.

The carbon body according to the invention may also be used as an anode in electrolytic production of various substances. Examples of this include an anode for the production of fluorine, which is required for the production of uranium hexafluoride in particular, an anode for the production of magnesium, sodium, lithium (melt-flow electrolysis) or an anode in chloralkali electrolysis.

Examples of other applications of the carbon body according to the invention include a heating pipe and/or ring, a plate heating element, a degassing pipe and/or a gas distributor system for nonferrous metal melting, a gasket, a diamond tool, a nozzle for high-voltage switches, graphite spheres for a pebble bed reactor, a component in the field of strand casting, compression casting, spin casting or railway wheel casting such as, for example, a casting mold, a solder or glass melting mold for use in the production of semiconductor housings, glass bushings and soldered joints.

The carbon body according to the invention is also used in the field of process technology. The carbon body according to the invention may be used as a component of a heat exchanger, for example, as a pipe bundle heat exchanger, a pipe tray, plate heat exchanger or gasket. In addition, the carbon body according to the invention may be used as a column, for example, in synthesis of acids, e.g., HCl synthesis, as a protective tube, a screen plate, a tunnel plate, a bell plate, a liquid distributor, a pore reactor, a pump or a rupture disk.

CLAIMS:

1. A carbon body that is produced by burning a mixture containing at least coke, wherein the coke has a degree of graphitization according to Maire and Mehring of 0.50 or less after a thermal treatment of the coke at 2800°C, calculated from the average layer spacing c/2, and wherein the grain of the coke is greater than 0.5 mm.

2. The carbon body according to claim 1, wherein the coke has a spherical morphology.

3. The carbon body according to claim 1 or 2, wherein the coke is contained in an amount of at most 25% by weight, based on the dry mixture.

4. The carbon body according to claim 3, wherein the coke is contained in an amount of 10% to 20% by weight, based on the dry mixture.

5. The carbon body according to any one of claims 1 to 4, wherein the coke has an onion skin structure.

6. The carbon body according to any one of claims 1 to 5, wherein the coke has a BET surface area of 20 to 40 m^2/g.

7. The carbon body according to any one of claims 1 to 6, which is a cathode block or a blast furnace brick.

8. The carbon body according to claim 7, wherein the cathode block is a graphitized cathode block.

9. A method for producing a carbon body comprising:

(a) mixing: (i) coke with anthracite, graphite or a mixture thereof, (ii) at least one binder selected from the group consisting of a petroleum-based binder, a carbon-based binder, a synthetic resin-based binder and a mixture thereof, and (iii) optionally, an additive;

(b) shaping the mixture from step (a) to a predetermined shape; and

(c) burning the shaped mixture from step (b) and, optionally, graphitizing the resultant burned molded body,

wherein the coke has a degree of graphitization according to Maire and Mehring of 0.50 or less after a thermal treatment of the coke at 2800°C, calculated from the average layer spacing c/2, and wherein the coke has a grain of greater than 0.5 mm.

10. The method according to claim 9, wherein the coke has a spherical morphology.

11. The method according to claim 9 or 10, wherein the coke is added in an amount of at most 25% by weight, based on the dry mixture.

12. The method according to claim 11, wherein the coke is added in an amount of 10 to 20 % by weight, based on the dry mixture.

13. The method according to any one of claims 9 to 12, wherein the coke has an onion skin structure.

14. The method according to any one of claims 9 to 13, wherein the coke has a BET surface area of 20 to 40 m^2/g.

15. Use of a carbon body according to any one of claims 1 to 8, as: a component in a machine, a chemical apparatus or a heat exchanger; a lining for a high-temperature component; or an electrode.

16. Use of a carbon body according to any one of claims 1 to 8, as: a cathode block in an electrolysis cell for producing aluminum; a blast furnace brick in a blast furnace for iron production; an electrode in carbothermal production of silicon; a lining for a blast furnace; a shaping tool; a lining for a melting and holding crucible or casting and tapping channels for producing aluminum, titanium, silicon, iron, iron alloys, phosphorus, glass or cement; an anode for production of fluorine; an anode for production of magnesium, sodium or lithium; an anode in chloralkali electrolysis, a heating tube and/or ring; a plate heating element; a degassing tube or gas distributor system for nonferrous metal melting; a gasket; a diamond tool; a nozzle for a high-voltage switch; graphite spheres for a pebble bed reactor; a casting mold in the field of strand casting, pressure casting, spin casting or railway wheel casting; a solder or glass melting mold in the production of semiconductor housing glass bushings and soldered joints; a tube bundle heat exchanger; a tube plate; a plate heat exchanger; a column; a protective tube; a perforated plate; a tunnel plate; a bell plate; a liquid distributor; a pore reactor; a pump; or a rupture disk.