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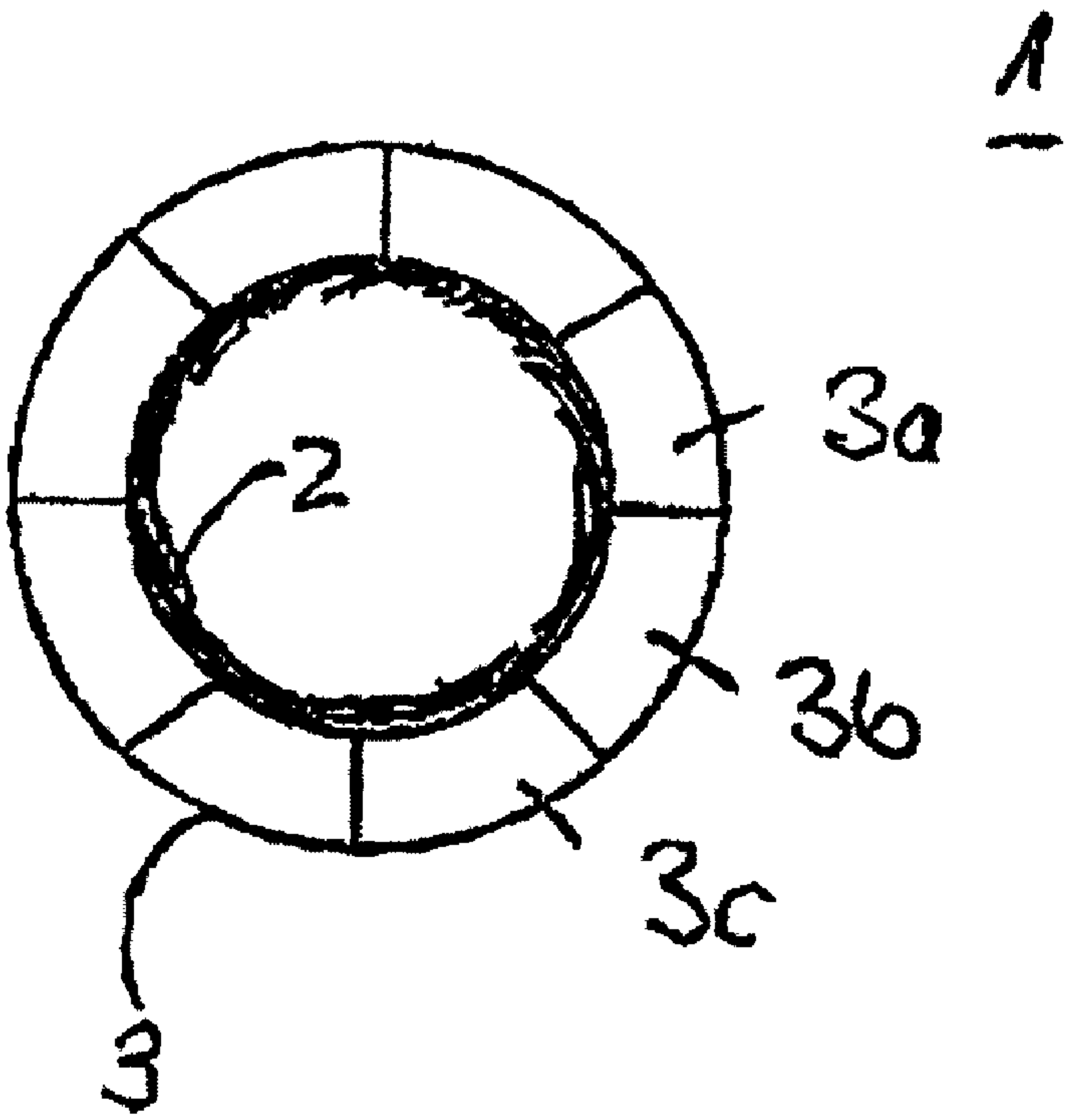
(54) Title: HIGH-TEMPERATURE-RESISTANT COMPOSITE



(57) Abrégé/Abstract:
The invention relates to high-temperature-resistant composites which comprise at least two layers of high-temperature-resistant carbon- or graphite-based materials of construction. The layers are joined to one another by a carbonized binder which contains planar anisotropic graphite particles.

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Abstract

The invention relates to high-temperature-resistant composites which comprise at least two layers of high-temperature-resistant carbon- or graphite-based materials of construction. The layers are joined to one another by a carbonized binder which contains planar anisotropic graphite particles.

High-temperature-resistant composite

The invention relates to high-temperature-resistant composites which are suitable for use in thermal insulations, heat shields, furnace internals, etc.

Materials of construction for high-temperature furnaces and reactors have to be both thermally insulating and resistant to high temperatures and inert toward the substances which react or are liberated in the interior of the furnace or reactor. Owing to their great heat stability, materials of construction based on carbon or graphite are frequently used for high-temperature applications, i.e. at temperatures above 800°C or even above 1000°C in a nonoxidizing atmosphere.

The heat loss to be avoided by means of the insulation can occur both by thermal radiation (predominantly at temperatures above 1000°C) and by thermal conduction and convection (predominantly at temperatures below 1000°C). Dense reflective materials are suitable for preventing thermal radiation and convection but on the other hand the thermal conductivity increases with increasing density. Materials having a relatively low density are suitable for suppressing thermal conduction but on the other hand are less suitable for preventing convection.

Thermal insulations are therefore preferably configured as layer composites which comprise at least one high-temperature-resistant material having a relatively low thermal conductivity (e.g. a felt composed of carbon fibers) for insulation against thermal conduction and a second, dense reflective material (e.g. graphite foil) for insulation against thermal radiation and convection. The denser material also contributes to the mechanical stability of the composite.

Graphite foil is particularly useful as a constituent of composites for thermal insulations since it is pliable and flexible and can thus be fitted to the round shapes typical of furnaces and reactors. In addition, graphite foil has a highly anisotropic thermal conductivity. Owing to the preferential thermal conduction in the plane of the foil, temperature equilibration occurs and local overheating (hot spots) in the insulation are avoided. Further advantages are the low fluid permeability and the reflective surface of graphite foil. Graphite foil typically has a thickness in the range from 0.3 to 1.5 mm and a density in the range from 0.4 to 1.6 g/cm^3.

Graphite foil is obtained in a known manner by compaction of graphite expanded by thermal shock treatment (graphite expandate).

The patent application WO 2004/063612 describes a thermally insulating composite comprising at least one layer of relatively highly compacted graphite expandate (density at least 0.4 g/cm^3, preferably from 0.5 to 1.6 g/cm^3) and at least one layer of less highly compacted graphite expandate (density less than 0.4 g/cm^3, preferably from 0.05 to 0.3 g/cm^3) which are joined to one another by a carbonized binder (carbonized phenolic resin, pitch or the like). The layer of more highly compacted graphite expandate is made as thin as the requirements for mechanical stability and impermeability permit (typically from 0.3 to 1.5 mm) and the layer of less highly compacted graphite expandate is made as thick as necessary for thermal insulation (typically from 5 to 20 mm). The structure can also be sandwich-like with two layers of more highly compacted graphite expandate enclosing a layer of less highly compacted graphite expandate. This stops particles from breaking away from the less highly compacted layer.

The production of the composite according to WO 2004/063612 comprises the main steps:

- production of at least one less highly compacted layer of graphite expandate and at least one more highly compacted layer of graphite expandate
- joining of the layers to one another, in which
  - the less highly compacted layer is coated with a carbonizable binder,
  - any solvents present are evaporated from the binder,
  - the more highly compacted layer is placed on the binder-coated less highly compacted layer and
  - the binder is carbonized by heat treatment in a nonoxidizing atmosphere at a temperature corresponding to at least the use temperature of the insulation material to be produced (typically from 800 to 1000°C).

WO 2004/092628 discloses a thermal insulation material which comprises at least one layer or a laminate of a plurality of layers of graphite foil and at least one layer of a thermally insulating carbon fiber reinforced carbon material which is isotropic in respect of the thermal conductivity. The thickness of the laminate of graphite foils is preferably up to 2 cm and the thickness of the isotropic insulating layer is from 1 to 10 cm at a density of preferably from 0.1 to 0.5 g/cm^3. The inner (i.e. facing the heat source) layer of graphite foil is reflective and prevents local over-heating. Owing to its low density, the outer layer reduces the loss of heat by thermal conduction.

The graphite foils to be laminated to one another are stacked on top of one another with a layer of a material which decomposes thermally to leave a carbon residue (e.g. Kraft paper) and has been coated on both sides with a carbonizable binder (e.g. phenolic resin) between each two graphite foils. The pores formed in the decomposition of the intermediate layers allow the gases liberated during curing and carbonization of the binder to escape. The laminate of graphite foils is joined to the layer of isotropic carbon fiber reinforced carbon by means of a carbonizable cement. The cement preferably comprises solvents and a polymerizable monomer together with carbon particles as filler in a proportion by volume of from 20 to 60%. Carbon black, pitch or milled coke, in each case having a particle size of less than 20 µm, were proposed as suitable carbon particles. In the formation of the bond between graphite foil laminate and the layer of carbon fiber reinforced carbon, the cement is firstly activated at a temperature of from 250°C to 300°C and subsequently carbonized by further heating to 800°C.

The bond between the layers consisting of various materials is critical for the reliable functioning of such layer composites. The bond has to ensure reliable cohesion but on the other hand must not result in significant thermal conduction between the layers to be joined.

A further problem is the buildup of stresses as a result of the different thermal expansion of the various materials.

According to the prior art, the bond between the layers of materials is achieved by means of a carbonizable binder which may, if appropriate, contain carbon particles as filler and is subsequently carbonized.

It has been found that the cohesion between the layers of various graphite- or carbon-based materials of construction can be improved when planar particles of graphite, e.g. natural graphite or compacted graphite expandate, which have a high anisotropy in respect of their crystal structure and their thermal conductivity are added to the carbonizable binder.

Further details, variants and advantages of the invention are indicated in the following comprehensive description, the figure and the examples.

Figure 1 schematically shows the cross section of a cylindrical component comprising an inner wound (rolled-up) layer and an outer layer made up of individual segments of pressed graphite expandate.

In contrast to conventional fillers such as milled coke, the particles added to the carbonizable binder according to the present invention are planar, i.e. their dimension in the flat area (diameter) is significantly greater than their thickness.

One filler which is suitable for the purposes of the invention is, for example, natural graphite whose particles are flake-like. An alternative is particles which are obtained by comminuting (cutting, milling, chopping or shredding) of graphite expandate which has been compacted to form planar structures (e.g. graphite foil). Offcuts which are inevitably obtained in the production of seals or other articles from graphite foil are advantageously utilized for this purpose. The particles obtained in this way are platelet-like.

The mean diameter of the particles added according to the invention to the carbonizable binder is from 1 to 250 µm; preference is given to particles having a mean diameter of from 5 to 55 µm.

In both variants of the particles added according to the invention to the carbonizable binder, i.e. both in the case of natural graphite flakes and in the case of the platelet-like particles obtained by comminuting of graphite foil, the typical layer plane structure of the graphite, which is responsible for the high anisotropy of the thermal conductivity which is typical of graphite, is present. The thermal conductivity along the layer planes, i.e. in the plane of the particles, is at least a factor of 10, preferably at least a factor of 20, higher than perpendicular to the layer planes. In the case of graphite foil, for example, the thermal conductivity perpendicular to the plane of the foil is only about 3-5 W/K*m, while the conductivity parallel to the plane of the foil reaches values in the range from about 100 W/K*m (at a density of 0.6 g/cm^3) to about 260 W/K*m (at a density of 1.5 g/cm^3).

Since the planar anisotropic particles in the binder layer are aligned parallel to the adjoining layers of material, the thermal conduction across the interface between the various materials is only low. In the case of milled coke as filler, the thermal conduction between the layers of material is suppressed to a lesser extent because of the more isotropic thermal conductivity of the coke.

A further advantageous effect of the planar graphite particles in the binder layer is that a binder layer containing such particles functions as stress equalization layer, i.e. mechanical stresses between the various materials joined to one another via the binder layer are reduced. It is assumed that this effect is attributable to the known lubricating action of graphite, but the invention is not tied to this explanation.

The mass of the particles is at least 5% of the mass of the binder used. Particle masses of from 10 to 30% of the binder mass have been found to be particularly useful, but the invention is not restricted to this range of values for the mass ratio of particles to binder.

As carbonizable binders, it is possible to use the binders known from the prior art, e.g. phenolic resins, furan resins, epoxy resins, pitch or the like. The curing, carbonization and, if appropriate, graphitization of the binder in the layer composites is carried out in a way known to those skilled in the art. Curing can, for example, be effected using the known vacuum bag process. The carbonization or graphitization occurs in a known manner at temperatures in the range from 800 to 2000°C.

The carbonizable binders containing planar anisotropic graphite particles are suitable for producing layer composites composed of various carbon or graphite materials which can be used for high-temperature applications or precursors thereof, for example layers of compacted graphite expandate of widely varying density (including graphite foil), hard carbon fiber felts, soft carbon fiber felts, carbon fiber reinforced carbon, fabric prepregs. The composites of the invention comprise at least two layers of high-temperature-resistant carbon- or graphite-based materials.

Depending on the application, a person skilled in the art will choose suitable materials according to their known specific advantages and join them according to the invention by means of a carbonizable binder containing planar anisotropic graphite particles (graphite flakes or platelets) to form a layer composite having the desired sequence of layers and subsequently carbonize the binder.

For the purposes of the present invention, carbon fibers are all types of carbon fibers regardless of the starting material, with polyacrylonitrile, pitch and cellulose fibers being the most widely used starting materials. In the carbon fiber reinforced carbon materials, the carbon fibers can be present as, for example, individual fibers, short fibers, fiber bundles, fiber mats, felts, woven fabrics or non-crimped fabrics, also combinations of a plurality of the fiber structures mentioned. The woven fabrics can comprise long fibers or carbon fibers which have been broken by drawing and respun (known as staple fibers).

Materials made up of carbon fibers or reinforced with carbon fibers contribute to the stiffness and strength of the composite. Layers having a low density, e.g. layers composed of carbon fiber felt or graphite expandate which in contrast to graphite foil is compacted only to a density of from 0.02 to 0.3 g/cm^3, have a particularly good thermally insulating effect because of their low thermal conductivity. A further advantage is their low weight.

The particular advantages of graphite foil for use in thermal insulations and the like have already been presented.

Suitable materials for the layer which directly adjoins the interior of the furnace, reactor or the like are graphite foil and also materials containing staple fibers. Owing to the drawing/breaking treatment, these fibers produce hardly any dust which could contaminate the interior of the furnace or reactor. The problem of dust formation by fine fibrils from conventional carbon fiber reinforced thermal insulations, which lead to contamination of the interior of the furnace or reactor to be insulated, is referred to in, for example, WO 2004/063612.

The production of, in particular, curved carbon fiber reinforced layers by the winding technique is known, cf. the European Patent EP 1 157 809 (corresponding to US patent US 6,641,693). Here, elongated (threads, yarns, rovings, ribbons or the like) or/and textile structures (woven fabrics, lay-ups, felts) composed of carbon fibers which may, if appropriate, be impregnated with a carbonizable binder are wound up on a shaping mandrel.

Curved layers comprising graphite foil can be produced by winding up a long sheet of graphite foil.

Between the various layers of material, a layer of the carbonizable binder containing planar anisotropic graphite particles is applied in each case. Thanks to the high viscosity of the binder containing planar anisotropic graphite particles, which is in the range from 20,000 to 30,000 mPa, this can be applied (e.g. applied by means of a spatula) without problems even to areas which are not horizontal, for example to curved surfaces as are typical of furnaces, reactors and pipes and are produced, for example, by the winding technique.

In the case of components which have to meet high demands in terms of mechanical stability, the layer composite preferably contains at least one layer which is cross-wound. This means that the wound layer contains strata which have been wound up at an opposed angle, e.g. +/- 45°C. Such layers can be obtained by winding up of elongated fiber structures such as threads, yarns, rovings or ribbons, with the fiber structures being able to be impregnated with a carbonizable binder. In the subsequent carbonization or graphitization, the binder which may be present in the wound fiber structures is carbonized or graphitized so as to produce a carbon fiber reinforced carbon material (CFRC).

It has been found to be advantageous for the surfaces to be joined to one another or at least the surface to which the binder is applied to be roughened.

It is also possible for individual components, e.g. tubes or plates, made of high-temperature-resistant carbon- or graphite-based materials of construction to be joined to one another to form complex components by means of the carbonizable binder containing planar anisotropic graphite particles, e.g. natural graphite flakes or platelets of compacted graphite expandate.

A specific variant of the invention relates to curved components, for example cylindrical insulations for furnaces or reactors. The winding technique is preferably used for producing these. However, some of the materials coming into question, for example graphite expandate which has been compacted to a density in the range from 0.02 to 0.3 g/cm^3, are not flexible enough to produce a layer of the corresponding material by winding a corresponding long sheet of material without the latter breaking. For this reason, it is proposed according to the invention that such curved layers be produced by assembling individual segments of the corresponding material. These segments are produced by means of customary shaping techniques, for example by pressing of graphite expandate in a mold corresponding to the shape of the segment to be produced or by cutting the segment from a block of pressed graphite expandate.

The cohesion between the segments within a layer is, like the cohesion between the individual layers, produced by use of a carbonizable binder to which planar anisotropic graphite particles have been added and which is subsequently cured and carbonized.

Figure 1 schematically shows the cross section of a cylindrical component 1 comprising an inner layer 2 which has been obtained, for example, by winding up a layer of graphite foil on a mandrel and an outer layer 3 which is made up of individual segments 3a, 3b, 3c … composed of pressed graphite expandate. A carbonizable binder to which planar anisotropic graphite particles had been added was applied both to the interface between layer 2 and layer 3 and also to the interfaces between the individual segments 3a, 3b, 3c.

Of course, further layers can be applied to the layer 3 composed of the segments 3a, 3b, 3c …, for example a stabilizing outer layer of wound-up carbon fibers.

Examples

Some combinations of materials which are joined by means of a carbonizable binder containing planar anisotropic graphite particles to form layer composites which are suitable for use in thermal insulations, heat shields, etc. are proposed below.

A first example of a composite according to the invention comprises a heat-reflecting inside (i.e. facing the interior of the furnace or reactor) layer of graphite foil, a layer of graphite expandate in which the graphite expandate is less highly compacted than in the graphite foil and which suppresses thermal conduction and a stabilizing outer layer of carbon fiber reinforced carbon (CFRC). The fiber reinforcement of the CFRC is formed either by a woven fabric or by layers of carbon fiber threads, yarns or rovings which are wound crosswise, e.g. at an angle of +/- 45°.

A second example of a composite according to the invention comprises a layer of pressed graphite expandate and a layer of CFRC.

A third example of a composite according to the invention comprises a sandwich made up of two layers of graphite foil which enclose a layer of less highly compacted graphite expandate.

Table 1 lists the typical thicknesses and densities of the individual materials.

Table 1

Material	Thickness/[mm]	Density/[g/cm^3]
Graphite foil	0.25-3	0.4-1.6
Less highly compacted graphite expandate	2-40	0.02-0.3
CFRC	0.2-0.75	1.15

Claims

1. A high-temperature-resistant composite comprising at least two layers of high-temperature-resistant carbon- or graphite-based materials which are joined to one another by a carbonized binder, characterized in that the binder contains planar anisotropic graphite particles.

2. The composite as claimed in claim 1, characterized in that the at least two joined layers each comprise one of the following materials: graphite foil, graphite expandate compacted to a density in the range from 0.02 to 0.3 g/cm^3, hard carbon fiber felt, soft carbon fiber felt, carbon fiber reinforced carbon.

3. The composite as claimed in claim 1, characterized in that the composite contains at least one curved layer (3) which comprises graphite expandate compacted to a density in the range from 0.02 to 0.3 g/cm^3 and is made up of individual segments (3a, 3b, 3c) which are joined to one another by a carbonized binder containing planar anisotropic graphite particles.

4. The composite as claimed in claim 1 or 3, characterized in that the planar anisotropic particles are flakes of natural graphite or particles obtained by comminuting of graphite expandate compacted to form planar structures.

5. The composite as claimed in claim 1 or 3, characterized in that the mean diameter of the planar anisotropic graphite particles is in the range from 1 to 250 µm.

6. The composite as claimed in claim 1 or 3, characterized in that the thermal conductivity in the planar anisotropic graphite particles along the layer planes

of the graphite is at least a factor of 10 higher than that perpendicular to the layer planes of the graphite.

7. The use of the composite as claimed in any of claims 1 to 6 in heat shields, thermal insulations, furnace internals and other high-temperature applications.

8. A process for joining layers or components of high-temperature-resistant carbon- or graphite-based materials, which comprises these steps:

- application of a carbonizable binder to which planar anisotropic graphite particles have been added to the surface of the first layer or the first component which is to be joined to the second layer or the second component
- application of the second layer or the second component to the binder-coated surface of the first layer or the first component
- curing of the binder
- carbonization or/and graphitization of the binder.

9. The process as claimed in claim 8, characterized in that the at least two layers joined to one another each comprise one of the following materials: graphite foil, graphite expandate compacted to a density in the range from 0.02 to 0.3 g/cm^3, hard felt, soft felt, carbon fiber reinforced carbon.

10. The process as claimed in claim 9, characterized in that at least one of the layers has been produced by winding of textile structures comprising carbon fibers or long sheets of graphite foil.

11. The process as claimed in claim 9, characterized in that at least one of the layers to be joined to one another is a curved layer (3) which comprises graphite expandate compacted to a density in the range from 0.02 to 0.3 g/cm^3 and is formed as follows

- production of individual segments (3a, 3b, 3c) which when assembled form the layer (3)
- joining of the segments by means of a carbonizable binder containing planar anisotropic graphite particles
- curing of the binder
- carbonization or/and graphitization of the binder.

12. The process as claimed in claim 8, characterized in that the components to be joined to one another are tubes or plates comprising carbon- or graphite-based materials.

13. The process as claimed in claim 8 or 11, characterized in that the planar anisotropic particles are flakes of natural graphite or particles obtained by comminuting of graphite expandate compacted to form planar structures.

14. The process as claimed in claim 8 or 11, characterized in that the mean diameter of the planar anisotropic graphite particles is in the range from 1 to 250 µm.

15. The process as claimed in claim 8 or 11, characterized in that the mass of the planar anisotropic graphite particles added to the binder is at least 5% of the mass of the binder.

16. The process as claimed in claim 8 or 11, characterized in that the thermal conductivity in the planar anisotropic graphite particles along the layer planes of the graphite is at least a factor of 10 higher than that perpendicular to the layer planes of the graphite.

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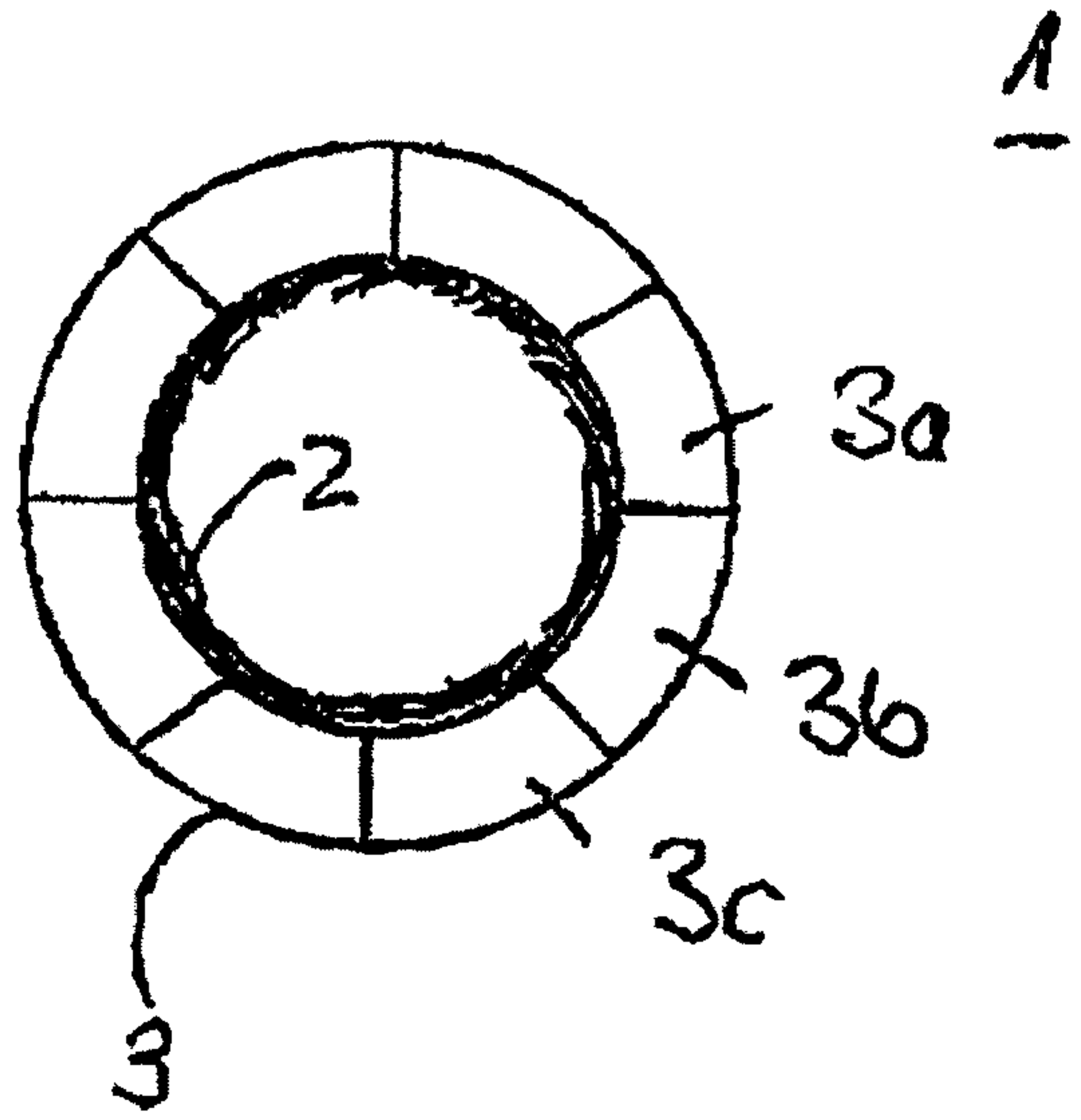
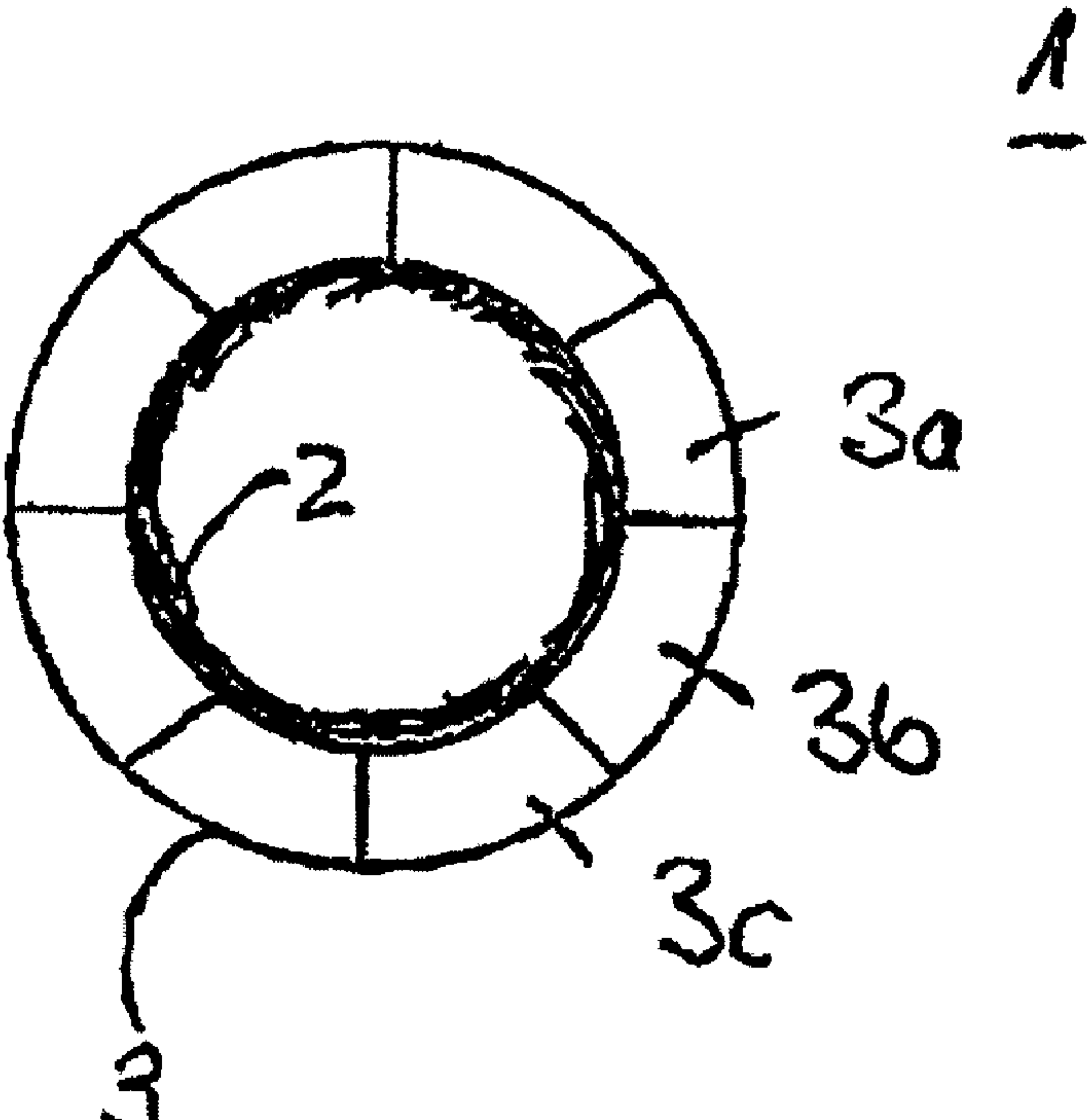
Figure 1

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