

METHOD FOR THE TREATMENT OF POROUS SUBSTRATES, AND
TREATED SUBSTRATE AND ITS USE

This invention relates to a method for treating porous substrates. In the method, at least one surface of a porous carbon-containing substrate is first provided with at least one silicon coating by applying at least one aqueous suspension comprising silicon particles, at least one binding agent, and water to the at least one surface and then subjecting it to a drying process. The at least one silicon coating is then subjected to at least one heat treatment in which the silicon coating melts to form a melt that infiltrates into the pores of the porous carbon-containing substrate, wherein silicon contained in the melt is at least partially converted to silicon carbide. Furthermore, the present invention also relates to a treated substrate and its use.

Carbon or graphite materials, including especially isostatically pressed graphite (iso-graphite) and carbon fiber reinforced carbon (CFC), are widely used in thermally highly stressed systems due to their good thermomechanical stability and ease of processing. These include components for high-temperature furnaces, such as heaters, insulation components, holders and crucibles. However, long-term contact with corrosive atmospheres or media under the influence of high temperatures and mechanical stress can lead to increased degradation of the carbon or graphite materials. This reduces the service life of the aforementioned components and leads to increased costs for maintenance and repair.

Carbon or graphite-silicon carbide composites (C/SiC composites) can be used to increase the service life. C/SiC composites are typically fabricated by infiltrating porous carbon or graphite bodies, e.g., carbon fiber reinforced carbon (CFC), with silicon melt (see, e.g., Manish Patel et al., Bulletin of Materials Science, 2012, 63-73). In this process, the component to be infiltrated is brought into contact with liquid silicon, which is absorbed by the component via capillary forces. Thus, reaction occurs between the carbon portion of the graphite and the liquid silicon and silicon carbide (SiC) is formed. The kinetics of the SiC formation reaction is determined by the contact angle and the spread of the silicon melt on or in the carbon or

graphite material (see O. Dezellus et al, Journal of Materials Science, 2005, 2307–2311). This can be influenced by external influences such as the gas atmosphere as well as the plant pressure during the process. In general, it must be noted that the increase in volume or differences in thermal expansion during SiC formation can create stresses in the component that lead to pronounced cracking in graphite materials with low mechanical stability (see R. Israel et al, J. Mater. Sci., 2010, 45, 2210–2217). The amount of silicon must also be precisely metered to ensure the most complete infiltration possible and at the same time prevent silicon residues on the surface after cooling. This is of fundamental importance in order to avoid costly post-processing or rejects. However, avoiding silicon residues is generally very difficult to achieve. Especially for dense graphite materials, as in the case of iso-graphite, infiltration by Si melt to seal the surface is unsuitable due to the low porosity and absorption capacity of liquid silicon.

Alternatively, a dense coating with a chemically inert and mechanically stable, usually ceramic component (e.g. SiC) can also be applied to the carbon or graphite materials. For this purpose, pyrolytic carbon or SiC is typically applied by means of chemical vapor deposition (CVD or chemical vapor infiltration CVI) (see, e.g., W. Zhou et al, Ceramics International 21730–21733). As a result, crack-free and high-density layers can generally be produced, which almost completely prevent the permeability of the carbon or graphite components to fluids or gases. If a material system is selected (e.g. SiC) that also brings a significant increase in mechanical or chemical resistance, the carbon or graphite material can be opened up for significantly more areas of application.

However, the above-mentioned methods are associated with high costs or great technical effort. In particular, homogeneous coatings on complex, large-area and three-dimensional components are very difficult to apply in both methods.

Based on this, it was the object of the present invention to provide a simple and cost-effective method for the treatment of porous substrates, with which substrates with a high resistance and a high surface quality can be obtained.

This object is solved with respect to a method for treating porous substrates with the features of patent claim 1 and with respect to a treated substrate with the features of patent claim 12. In patent claim 18, possible uses of the treated substrate according to the invention are indicated. The dependent
5 claims represent advantageous further developments.

According to the invention, a method for the (surface) treatment of porous substrates is thus provided, in which

- 10 a) at least one surface of a porous carbon-containing (or carbonaceous) substrate is provided with at least one silicon coating by applying at least one aqueous suspension comprising silicon particles, at least one binding agent and water to the at least one surface and thereafter subjecting it to a drying process, and
- 15 b) the at least one silicon coating is subjected to at least one heat treatment in which the silicon coating melts into a melt which infiltrates into the pores of the porous carbon-containing (or carbonaceous) substrate, silicon contained in the melt being at least partially converted into silicon carbide.

In step a) of the method according to the invention, at least one surface of a porous carbon containing (or carbonaceous) substrate is provided with at
20 least one silicon coating. For this purpose, at least one aqueous suspension is applied to the at least one surface and then the applied at least one aqueous suspension is subjected to a drying process. The at least one aqueous suspension comprises silicon particles, at least one binding agent, and water. Preferably, the at least one aqueous suspension may also consist of silicon
25 particles, at least one binding agent, and water. Preferably, the silicon particles contained in the at least one aqueous suspension are silicon granules or silicon powder, particularly preferably silicon granules. Preferably, the at least one aqueous suspension is applied in layers to the at least one surface.

In this context, a binding agent can generally be understood as a substance
30 that creates or promotes chemical bonds at phase boundaries of other substances or triggers or increases effects such as cohesion, adsorption and adhesion or friction.

The at least one binding agent causes an increase in the viscosity and yield point of the aqueous suspension so that it adheres to the at least one surface after being applied thereto.

5 The drying process can remove the water contained in the applied at least one aqueous suspension, resulting in a silicon coating disposed on the at least one surface comprising the silicon particles and the at least one binding agent, wherein the silicon particles are further fixed to the at least one surface by the at least one binding agent. The at least one binding agent can thus prevent the silicon particles from slipping on or falling off the at least one surface during or after the drying process (e.g., during transport of the substrate or due to an at least partially vertical, sloped or non-planar orientation of the at least one surface). In other words, the at least one binding agent can be used to ensure that the silicon coating present after the drying process is abrasion-resistant and adhesive. The distribution of the silicon particles on the at least one surface obtained during the application of the at least one suspension is thus maintained during or after the drying process (until melting in step b) of the method according to the invention) due to the at least one binding agent.

20 In step b) of the method according to the invention, the at least one silicon coating obtained in step a) of the method according to the invention is then subjected to at least one heat treatment. During this heat treatment, the silicon coating melts into a molten mass that infiltrates into the pores of the porous carbon containing (or carbonaceous) substrate. The area(s) of the substrate into which the melt infiltrates can be referred to as the infiltration zone. In addition, silicon contained in the melt is at least partially converted into silicon carbide during heat treatment. Preferably, silicon contained in the melt is substantially completely, preferably completely, converted to silicon carbide during the heat treatment.

30 Due to the (at least partial) conversion of the silicon into silicon carbide, the pores of the finally obtained substrate in the infiltration zone are at least partially filled with silicon carbide. As a consequence, an almost complete closure, preferably an essentially complete closure, of the pores near the treated surface by chemically stable silicon carbide can be achieved (if the infiltration depth is sufficiently high), and thus an almost complete sealing,

preferably an essentially complete sealing, of the treated surface of the substrate can be achieved, as evidenced by only a low permeability of the substrates obtained by the method according to the invention and only a low open porosity in the infiltration zone of the substrates obtained by the method according to the invention. The degree of sealing of the treated surface depends on the infiltration depth, i.e. the thickness of the infiltration zone. It should be noted that the degree of sealing achieved at a given depth of infiltration depends on the material and the properties of the substrate. Thus - depending on the material - a different depth of infiltration may be necessary to achieve a certain degree of sealing of the surface. The thickness of the infiltration zone (or the infiltration depth) and thus the degree of sealing can be adjusted by various parameters (such as the amount per unit area of the at least one aqueous suspension applied to the at least one surface, the proportion of silicon particles in the at least one aqueous suspension, the gas atmosphere during the at least one heat treatment, the temperature during the at least one heat treatment, the duration during the at least one heat treatment, and/or the process pressure during the at least one heat treatment). The thickness of the infiltration zone (or the infiltration depth) can be, for example, at least 50 μm , preferably at least 100 μm , particularly preferably, at least 200 μm . The degree of sealing can be determined by the permeability of the substrate as well as by the open porosity in the infiltration zone. The lower the permeability of the substrate and the lower the open porosity in the infiltration zone, the higher the degree of sealing.

The method according to the invention is particularly characterized by the fact that the use of an aqueous suspension comprising silicon particles, at least one binding agent and water enables a very defined silicon application, by means of which both the most complete possible sealing of the treated surface can be achieved and the formation of silicon residues on the surface of the substrate can be at least largely avoided. A particular advantage of the method according to the invention is that even with very dense and thus poorly infiltratable materials or substrates, the treated surface can be sealed as completely as possible and the formation of silicon residues on the surface of the substrate can be at least largely avoided.

In the method according to the invention, the very defined silicon application is achieved by applying the silicon particles to the at least one surface of the substrate with the aid of an aqueous suspension which additionally contains at least one binding agent. By applying the silicon particles with the aid of an aqueous suspension, a very homogeneous distribution of the silicon particles on the at least one surface of the substrate can be achieved, whereby the aqueous suspension adheres to the at least one surface due to the at least one binding agent. In addition, the at least one binding agent ensures that the silicon particles continue to be fixed to the at least one surface after removal of the water (by the drying process), so that the highly homogeneous distribution of the silicon particles is maintained even after removal of the water, even if the substrate is transported during the process or if the at least one surface is at least partially vertical, oblique or non-planar. This ensures that the very homogeneous distribution of the silicon particles is maintained until the particles melt. Due to the homogeneous distribution of the silicon particles, a very defined application of the silicon is finally achieved. This very defined application makes it possible, on the one hand, to apply a sufficiently high amount of silicon (with the aid of the aqueous suspension) at the individual points of the surface to be treated, so that ultimately a sufficient sealing of the surface or a sufficient closure of the pores near the surface can be achieved, and on the other hand, the absorption volume of the pores for the silicon melt is not exceeded, so that silicon residues on the treated surface can be at least largely avoided. The very defined silicon deposition is particularly advantageous for very dense and thus poorly infiltratable materials or substrates.

The substrates obtained by the process of the invention exhibit both increased hardness and wear resistance due to the presence of the silicon carbide in the pores in the infiltration zone of the substrate. For this reason alone, the resistance of the substrates obtained by the method according to the invention is greatly increased.

Furthermore, since an almost or essentially complete sealing of the treated surface or an almost or essentially complete closure of the pores near the surface can be achieved, a penetration of gases or fluids into the material and, accordingly, an interaction with corrosive media (e.g. oxygen), which would lead to degradation of the carbon material of the substrate, can be prevented

in this way. This also contributes to the high resistance of the substrates obtained by the method according to the invention.

5 It should be emphasized here that the method according to the invention can achieve a better or more complete sealing of the treated surface than the methods known from the prior art, such as methods in which a coating is applied by means of CVI. As a result, the method according to the invention can be used to obtain substrates that have a lower permeability and that have a lower open porosity in the infiltration zone than substrates treated according to the prior art.

10 In addition, the method according to the invention also achieves a better or more complete sealing of the treated surface than with processes in which coating is carried out by applying silicon particles without using a suspension or coating is carried out using a suspension with silicon particles but without water and/or binding agent. Consequently, the method according to the
15 invention can be used to obtain substrates which have a lower permeability and which have a lower open porosity in the infiltration zone than substrates which have been treated according to processes in which coating is carried out by applying silicon particles without using a suspension or coating is carried out using a suspension with silicon particles but without water and/or
20 binding agent.

At the same time, the substrates obtained by the method according to the invention are characterized by a high surface quality, without the need for costly post-processing. Thus, in the method according to the invention, the use of an aqueous suspension comprising silicon particles, at least one binding
25 agent and water enables a very defined silicon application, by means of which the deposition of silicon residues on the surface of the substrate, which would lead to a reduction in the surface quality, can be at least largely avoided. In addition, costly post-processing to remove such silicon residues (e.g. an additional grinding or abrasive step to remove the silicon residues) can also be
30 dispensed with.

Since the method according to the invention does not require complex coating processes and technologies, such as CVD processes, and, in addition, post-processing of the substrates to remove silicon residues is not necessary,

the method according to the invention can be carried out in a simple manner and is also cost-effective.

Thus, the method according to the invention discloses a simple and inexpensive process for the treatment of porous substrates, with which
5 substrates with a high resistance and a high surface quality can be obtained.

A preferred variant of the method according to the invention is characterized by the fact that the silicon particles have a mean particle size (d50 value) in the range from 10 μm to 3500 μm , preferably from 310 μm to 1700 μm , particularly preferably from 500 to 1000 μm . With such an average particle
10 size of the silicon particles, silicon residues on the treated surface can be avoided even better, so that the substrate obtained has an even higher surface quality. In particular, with a particle size of at least 310 μm , preferably of at least 500 μm , the silicon particles can be melted even more effectively during the infiltration process and the resulting melt can be distributed even
15 more efficiently on the surface to be treated. Thus, with the appropriate dosage, the silicon melt can be completely absorbed by the graphite substrate without leaving any residue and covering the entire surface. In this way, silicon residues on the treated surface can be completely avoided, so that an even higher surface quality is obtained without the need for post-processing
20 to remove silicon residues.

The average particle size (d50 value) of the silicon particles can be determined, for example, by means of laser diffraction (e.g. according to ISO 13320:2020-01).

A further preferred variant of the method according to the invention is
25 characterized in that the silicon particles have an average particle size (d50 or d50 value) of more than 500 μm and up to 3500 μm , preferably in the range from 550 μm to 3500 μm , particularly preferably in the range from 650 μm to 1700 μm , most preferably in the range from 750 μm to 1000 μm . The average particle size (d50 or d50 value) of the silicon particles can be determined, for
30 example, by means of laser diffraction (e.g. according to ISO 13320:2020-01). A particle size of the silicon particles of more than 500 μm enables an even more efficient melting of the silicon particles during the infiltration process than a smaller average particle size of up to 500 μm . Surprisingly, it was found

that a higher particle size of the silicon particles leads to a more efficient melting of the silicon particles. In particular with an average particle size of more than 500 μm and up to 3500 μm , e.g. in the range from 550 μm to 3500 μm , a complete melting of the silicon particles can be ensured so that the silicon (with the appropriate dosage) can be absorbed by the substrate without leaving any residue. In this way, a highly crystalline and also crack- and pore-free surface can be obtained. This ultimately results in an outstanding surface quality without the need for post-processing to remove silicon residues.

Basically, it was surprisingly found that finer Si material tends to have a lower ability to complete melting. A decisive aspect here is the high specific surface which typically increases with the decrease in particle size. On the one hand, in the case of Si, it comes to an increase oxidation of the surface in air but also in contact with water during the preparation or processing of the suspension. The resulting silicon oxide layer on the particle surface impairs in the following the formation of a molten phase and thus inhibits the infiltration process. In order to avoid this, the oxide layer can be removed from the powder using chemical (e.g. treatment with hydrofluoric acid HF) or thermal processes. However, this is a complex process and cannot be implemented in the case of a Si-based coating. Furthermore, a high specific surface can react with free carbon from the furnace atmosphere or residues of the carbon-based organic suspension additives (e.g. binders) to form SiC close to the surface before the actual melting. The melting of the particles thus only takes place partially and not completely and cracked and porous structures remain.

A further preferred variant of the method according to the invention is characterized in that the silicon particles

- have an average particle size (d_{50} or d_{50} value) of 800 μm , or
- have an average particle size (d_{50} or d_{50} value) of more than 500 μm and up to 3500 μm , preferably in the range from 550 μm to 3500 μm , particularly preferably in the range from 650 μm to 1700 μm , most preferably in the range from 750 μm to 1000 μm , wherein the average particle size (d_{50} or d_{50} value) of the silicon particles is not 800 μm .

A further preferred variant of the method according to the invention is characterized in that the silicon particles

- 5 - have an average particle size (d50 or d50 value) of more than 500 μm and less than 800 μm , preferably of at least 550 μm and less than 800 μm , particularly preferably of at least 650 μm and less than 800 μm , most preferably of at least 700 μm and less than 800 μm , or
- have an average particle size (d50 or d50 value) of 800 μm , or
- 10 - have an average particle size (d50 or d50 value) of more than 800 μm and up to 3500 μm , preferably of more than 800 μm and up to 1700 μm , more preferably of more than 800 μm and up to 1000 μm .

The average particle size (d50 or d50 value) of the silicon particles can be determined, for example, by means of laser diffraction (e.g. according to ISO 13320:2020-01).

15 A further preferred variant of the method according to the invention is characterized in that the silicon particles have an oxidation tendency that is characterized by that when the silicon particles come into contact with water over a period of 24 hours, a quantity of hydrogen (H_2) is released that is less than $5 \cdot 10^{-5}$ vol%. The measurement can be carried out, for example, using a hydrogen measuring probe at a distance of 1 cm from the surface of the suspension. Thus, the silicon particles have a very low oxidation tendency (on 20 contact with water). The oxidation tendency on contact with water can be determined via the release of hydrogen (H_2). According to the reaction $\text{Si} + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2 \text{H}_2$, the water molecule is split during the oxidation of Si. This reaction is further favored with increasing specific surface or decreasing 25 particle size.

A further preferred variant of the method according to the invention is characterized in that the at least one binding agent

- ensures an adhesive strength of the silicon coating of at least 0.15 MPa, and/or
- 30 - is selected from the group consisting of polyvinyl alcohol, polyethylene glycol, polyvinyl butyral, polyacrylic acid, polyurethane, chloroprene

rubber, phenolic resin, acrylic resin, cellulose, cellulose derivatives, alginic acid, dextrin, and mixtures thereof.

The adhesion strength of the silicon coating can be determined, for example, by means of a peel test according to DIN EN ISO 4624:2016-08.

5 Preferably, the at least one binding agent is at least one organic binding agent. Particularly preferably, the at least one binding agent is selected from the group consisting of polyvinyl alcohol, polyethylene glycol, polyvinyl butyral, polyacrylic acid, polyurethane, chloroprene rubber, phenolic resin, acrylic resin, cellulose, cellulose derivatives, alginic acid, dextrin, and mixtures thereof. Such a binding agent can achieve a particularly high adhesion strength of the silicon coating.

The cellulose derivatives are preferably selected from the group consisting of cellulose ether, methyl cellulose, carboxymethyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, and mixtures thereof.

15 For example, the product "Peptapon 520" from Zschimmer & Schwarz Chemie GmbH can be used as a binding agent.

A further preferred variant of the method in accordance with the invention is characterized in that the at least one aqueous suspension

- 20 - contains 1 to 50% by weight, preferably 5 to 35% by weight, of the silicon particles, based on the total weight of the at least one aqueous suspension, and/or
- contains 0.01 to 10% by weight, preferably 0.03 to 3% by weight, particularly preferably 0.05 to 0.3% by weight, of the at least one binding agent, based on the total weight of the at least one aqueous suspension.

25 The amount of silicon applied can be varied via the proportion of silicon particles in the at least one aqueous suspension. By using 0.01 to 3% by weight, preferably 0.05 to 0.3% by weight, of the at least one binding agent, based on the total weight of the at least one aqueous suspension, a particularly advantageous adhesive effect can be achieved.

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According to a further preferred variant of the method according to the invention, the application of the at least one aqueous suspension in step a) is carried out by means of dipping, brushing, doctoring and/or spray application. The application of the at least one aqueous suspension particularly preferably takes place by means of spray application in step a). With these methods, flat as well as three-dimensional and complex components can be homogeneously provided with the at least one aqueous suspension in a particularly simple manner. A particularly homogeneous application is possible by spray application. In addition, with the methods mentioned, in particular with spray application, the applied suspension quantity and thus the silicon quantity per unit area can be adjusted in a very defined manner, enabling an even more defined application of the at least one aqueous suspension and thus of the silicon quantity. The amount of suspension applied can also be influenced by the number of coating cycles.

Preferably, by the application of the at least one aqueous suspension in step a), a silicon amount (or an amount of silicon particles) of 0.003 to 0.5 g/cm², preferably of 0.01 to 0.2 g/cm², more preferably of 0.02 to 0.1 g/cm², most preferably of 0.03 to 0.08 g/cm², in particular of 0.04 to 0.07 g/cm², is applied to the at least one surface.

Preferably, in step a), an amount of the aqueous suspension from 0.001 g/cm² to 1.5 g/cm², preferably from 0.005 g/cm² to 0.5 g/cm², more preferably from 0.06 g/cm² to 0.4 g/cm², is applied to the at least one surface.

A further preferred variant of the method according to the invention is characterized in that the drying process is carried out at a temperature in the range from 10 °C to 200 °C, preferably from 80 °C to 100 °C, and/or over a duration of 5 h to 48 h, preferably from 10 h to 12 h.

A further preferred variant of the method according to the invention is characterized in that the at least one heat treatment

- takes place at a temperature in the range from 1400 °C to 1800 °C, preferably from 1450 °C to 1550 °C, and/or
- takes place over a period of 1 h to 10 h, preferably 4 h to 6 h, and/or
- takes place under
 - o vacuum or

- 5 o inert gas atmosphere, preferably argon atmosphere, at a (process) pressure of from 10 mbar to 2000 mbar, preferably from 100 mbar to 1800 mbar, particularly preferably from 500 mbar to 1500 mbar, most preferably from 800 mbar to 1200 mbar.

A further preferred variant of the method according to the invention is characterized in that the at least one heat treatment

- 10 - takes place at a temperature in the range from 1400 °C to 1800 °C, preferably from 1450 °C to 1550 °C, and/or
- takes place over a period of 1 h to 10 h, preferably 4 h to 6 h, and/or
- takes place under inert gas atmosphere, preferably argon atmosphere, and/or
- 15 - takes place at a (process) pressure of from 10 mbar to 2000 mbar, preferably from 100 mbar to 1800 mbar, particularly preferably from 500 mbar to 1500 mbar, most preferably from 800 mbar to 1200 mbar.

20 By varying the gas atmosphere, temperature, duration and/or process pressure, the thickness of the infiltration zone (or infiltration depth) and thus the degree of sealing can be influenced and adjusted.

A further preferred variant of the method in accordance with the invention is characterized in that

- 25 - the porous carbon-containing (or carbonaceous) substrate comprises or consists of a material selected from the group consisting of graphite, preferably iso-graphite; carbon fiber reinforced carbon; silicon carbide fiber reinforced carbon; silicon carbide fiber reinforced silicon carbide; glassy carbon; sintered silicon carbide; silicon infiltrated silicon carbide; and combinations thereof, and/or
- 30 - the porous carbon-containing (or carbonaceous) substrate comprises or consists of a material having a coefficient of thermal expansion (or thermal expansion coefficient) of at least $2.0 \cdot 10^{-6} \text{ K}^{-1}$, preferably of at

least $2.8 \cdot 10^{-6} \text{ K}^{-1}$, more preferably of at least $3.0 \cdot 10^{-6} \text{ K}^{-1}$, most preferably of at least $3.2 \cdot 10^{-6} \text{ K}^{-1}$, and/or

- the porous carbon-containing (or carbonaceous) substrate has an open porosity, measured by mercury porosimetry, of at least 12%, preferably from 12% to 30%, more preferably from 14% to 25%, most preferably from 15% to 20%, and/or
- the pores of the porous carbon-containing (or carbonaceous) substrate have an average pore diameter in the range from $0.1 \text{ }\mu\text{m}$ to $100 \text{ }\mu\text{m}$, preferably from $0.1 \text{ }\mu\text{m}$ to $10 \text{ }\mu\text{m}$, particularly preferably from $1 \text{ }\mu\text{m}$ to $5 \text{ }\mu\text{m}$, most preferably from $1.5 \text{ }\mu\text{m}$ to $5 \text{ }\mu\text{m}$.

The porous carbon-containing (or carbonaceous) substrate preferably contains graphite, particularly preferably iso-graphite.

Preferably, the porous carbon containing (or carbonaceous) substrate is a porous graphite substrate, more preferably a porous iso-graphite substrate. The method according to the invention is particularly advantageous for graphite substrates, especially iso-graphite substrates, since these have a high density and are therefore difficult to infiltrate. The method according to the invention can also be used to treat these substrates without any problems due to the very defined application of the aqueous suspension and the resulting advantages.

Iso-graphite is graphite produced by the isostatic pressing process.

For example, the porous substrate may be a crucible, preferably a graphite crucible, most preferably an iso-graphite crucible.

Preferably, the porous carbon-containing (or carbonaceous) substrate includes or consists of a material having a coefficient of thermal expansion (or thermal expansion coefficient) of at least $2.8 \cdot 10^{-6} \text{ K}^{-1}$, preferably of at least $3.0 \cdot 10^{-6} \text{ K}^{-1}$, more preferably of at least $3.2 \cdot 10^{-6} \text{ K}^{-1}$. In this way, the risk of cracking and deformation of the substrate during the process can be reduced.

The coefficient of thermal expansion (or thermal expansion coefficient) can be determined, for example, according to DIN 51909:2009-05.

Infiltration of liquid silicon into a carbon-containing substrate generally results in the chemical reaction of silicon and carbon to form silicon carbide (SiC) and consequently SiC is formed in the pores. With the associated increase in volume during SiC formation, mechanical stresses are induced in the carbon-containing material, which increase with increasing infiltration depth. In addition, as the difference between the thermal expansion coefficients of the carbon-containing material and SiC increases, thermal stresses can also occur during heat treatment. If the mechanical stability of the carbon-containing material is exceeded, cracks may form in the substrate and thus destroy the component. By using a carbon-containing material with a high mechanical stability, e.g. characterized by a high flexural strength and/or a high compressive strength, the risk of cracking and deformation of the substrate can be reduced. Similarly, the risk of cracking and deformation of the substrate can be reduced if the carbon-containing material has a suitable coefficient of thermal expansion, i.e. a coefficient of thermal expansion with as little difference as possible from the coefficient of thermal expansion of silicon carbide.

Preferably, the porous carbon-containing (or carbonaceous) substrate comprises or consists of a material having a flexural strength of at least 30 MPa, preferably of at least 45 MPa, more preferably of at least 50 MPa, most preferably of at least 60 MPa, in particular of at least 70 MPa, and/or a compressive strength of at least 50 MPa, preferably of at least 90 MPa, more preferably of at least 110 MPa, most preferably of at least 130 MPa, in particular of at least 140 MPa.

It is preferred that the porous carbon-containing (or carbonaceous) substrate has an open porosity, measured by mercury porosimetry, of at least 12%, preferably from 12% to 30%, more preferably from 14% to 25%, most preferably from 15% to 20%, and/or the pores of the porous carbon-containing (or carbonaceous) substrate have an average pore diameter in the range from 0.1 μm to 10 μm , preferably from 1 μm to 5 μm , more preferably from 1.5 μm to 5 μm . In this way, a particularly good sealing of the pores near the surface or a particularly good sealing of the treated surface can be achieved, which is shown by a very low permeability of the substrate as well as only a very low open porosity in the infiltration zone. In this context, it is particularly advantageous if the porous carbon-containing (or carbonaceous)

5 substrate has an open porosity, measured by mercury porosimetry, of at least 12%, preferably from 12% to 30%, more preferably from 14% to 25%, most preferably from 15% to 20%, and the pores of the porous carbon-containing (or carbonaceous) substrate have an average pore diameter in the range from 0.1 μm to 10 μm , preferably from 1 μm to 5 μm , more preferably from 1.5 μm to 5 μm .

The open porosity of the porous carbon-containing (or carbonaceous) substrate is determined by mercury porosimetry (e.g. according to DIN 66133:1993-06).

10 The mean pore diameter of the pores of the porous carbon-containing (or carbonaceous) substrate can be determined, for example, by mercury porosimetry (e.g. according to DIN 15901-1:2019-03).

Preferably, the infiltration depth of the melt (or the thickness of the infiltration zone) is adjusted by

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- the amount per unit area of the at least one aqueous suspension applied to the at least one surface, and/or
 - the proportion of silicon particles in the at least one aqueous suspension, and/or
 - the gas atmosphere during the at least one heat treatment, and/or
- 20
- the temperature during the at least one heat treatment, and/or
 - the duration during the at least one heat treatment, and/or
 - the process pressure during the at least one heat treatment.

The degree of sealing of the treated surface can be adjusted via the thickness of the infiltration zone or the infiltration depth of the melt.

25 According to a further preferred variant of the method according to the invention, the infiltration depth of the melt (or the thickness of the infiltration zone) is adjusted by the amount per unit area of the at least one aqueous suspension applied to the at least one surface and/or by the pressure during the at least one heat treatment. The degree of sealing of the treated surface

30 can be adjusted via the thickness of the infiltration zone or the infiltration depth of the melt.

According to a particularly preferred process variant, the infiltration depth of the melt (or the thickness of the infiltration zone) is adjusted by the pressure of the atmosphere, preferably the argon atmosphere, during the at least one heat treatment. Here, infiltration depth can also be influenced independently of the carbon-containing material by selecting the appropriate process pressure.

A further preferred variant of the method according to the invention is characterized in that, after step b), at least one aqueous suspension comprising at least one refractory metal carbide (e.g. tantalum carbide) and water is applied to the at least one surface of the carbon-containing substrate and the substrate is then subjected to a sintering process.

A further preferred variant of the method according to the invention is characterized in that,

- the porous carbon-containing (or carbonaceous) substrate is doped with at least one dopant selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorus (P), vanadium (V), scandium (Sc), gallium (Ga), indium (In), germanium (Ge), tin (Sn), lead (Pb), arsenic (As), antimony (Sb), bismuth (Bi), and mixtures thereof, wherein the at least one dopant is preferably selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorous (P), vanadium (V), scandium (Sc), and mixtures thereof, and/or
- the silicon particles are doped with at least one dopant selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorus (P), vanadium (V), scandium (Sc), gallium (Ga), indium (In), germanium (Ge), tin (Sn), lead (Pb), arsenic (As), antimony (Sb), bismuth (Bi), and mixtures thereof, wherein the at least one dopant is preferably selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorous (P), vanadium (V), scandium (Sc), and mixtures thereof, and/or
- the at least one aqueous suspension additionally comprises at least one (powdered and/or water-soluble) compound containing at least one dopant selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorus (P), vanadium (V), scandium

(Sc), gallium (Ga), indium (In), germanium (Ge), tin (Sn), lead (Pb), arsenic (As), antimony (Sb), bismuth (Bi), and mixtures thereof, wherein the at least one dopant is preferably selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorous (P), vanadium (V), scandium (Sc), and mixtures thereof, and/or

- the at least one heat treatment is carried out in the presence of a process gas containing or consisting of nitrogen.

In this way, at least one dopant or dopant element is incorporated into the silicon carbide formed in step b), i.e. the silicon carbide is doped with the at least one dopant. The at least one (powdered and/or water-soluble) compound is preferably at least one (powdered and/or water-soluble) salt.

By the incorporation of one or more dopants or dopant elements into the (e.g. polycrystalline) silicon carbide formed in step b), the electrical and/or thermal properties of the produced treated substrate can be varied or specifically adjusted. Material characteristics that can be adjusted with this are, for example, the (specific) resistance, the electrical conductivity and the thermal conductivity of the silicon carbide. Depending on selection and concentration of the respective dopant element, the electrical properties and the thermal properties can also be adjusted independently of each other.

The doping of the silicon carbide can be achieved in various ways, namely via the silicon particles, via the carbon-containing (or carbonaceous) substrate, via an additional compound present in the suspension, and/or via a process gas. For example, on the one hand, silicon (Si) doped with the respective dopant(s) can be used as starting material for the infiltration process, i.e. the used silicon particles are doped with the corresponding dopant(s). In principle, some of the silicon carbide dopants listed, such as B, P, N, Ga, As, Sb and Al, are also established in Si crystal growing and such doped material is available in a wide variation of dopant concentrations. With the melting and the formation reaction of silicon carbide during the infiltration, the dopants introduced via the silicon material can also be incorporated into the resulting silicon carbide. In the case of nitrogen (N), the introduction can also take place via the gas phase. If N (or N₂) is used as a process gas during the

infiltration process in the presence of a molten Si phase or is proportionally mixed into the process gas, N is dissolved in the melt.

Another possibility is to introduce the corresponding dopant(s) into the coating suspension in the form of (powdered and/or water-soluble) compounds (e.g. salts). Using the spraying process, these can be distributed homogeneously on the substrate surface in the same way as the Si material and dissolved in the liquid Si during the melting process or absorbed directly as a dopant during the formation reaction of silicon carbide.

Additionally, the starting material of the carbon-containing (or carbonaceous) substrate (e.g. graphite) can be provided with the corresponding dopant(s) in advance of the silicon coating process. These can, for example, be mixed with the raw materials during the actual manufacturing process of the substrate material or the processed substrate material can be impregnated with dopant compounds by means of a solution, a colloid or a suspension. During the reaction of the silicon melt with the substrate material, these can then be incorporated into the Si melt and/or the resulting silicon carbide.

A general advantage of the production of doped silicon carbide by means of silicon infiltration is also that possibly a more homogeneously p-type doping can be achieved, which cannot be achieved in crystal growing using conventional methods. Preferably, the at least one dopant can therefore be at least one p-type dopant, which is particularly preferably selected from the group consisting of aluminum (Al), boron (B), vanadium (V), scandium (Sc), gallium (Ga), indium (In), and mixtures thereof, wherein the at least one p-type dopant is particularly preferably selected from the group consisting of aluminum (Al), boron (B), vanadium (V), scandium (Sc), and mixtures thereof.

Furthermore, there is also the possibility, e.g. by using the suspension based spraying process, to provide defined substrate regions only locally with silicon coatings containing dopants. In this way, defined areas with and without doping or areas with different dopant concentrations or dopant elements can also be generated within a component.

The present invention also relates to a substrate or (surface) treated substrate comprising a carbon-containing (or carbonaceous) substrate material with pores, wherein the substrate has on at least one surface an infiltration zone in

5 which the pores of the substrate material are at least partially filled with silicon carbide, wherein the substrate or treated substrate has a (gas) permeability of at most $5 \cdot 10^{-15} \text{ m}^2$, and wherein the substrate or treated substrate has an open porosity, determined by mercury porosimetry, of at most 10% in the infiltration zone.

The (gas) permeability of the treated substrate can be determined, for example, by means of differential pressure methods (e.g. according to EN 993-4 : 1995).

10 The open porosity in the infiltration zone of the treated substrate is determined by mercury porosimetry (e.g. according to DIN 66133:1993-06).

15 The infiltration zone is ultimately the area(s) of the treated substrate where silicon carbide is present in the pores of the substrate material. In the area(s) of the treated substrate outside the infiltration zone, no silicon carbide is present in the pores of the substrate material. Thus, the infiltration zone extends from the at least one surface of the treated substrate to the location(s) of the treated substrate furthest from the at least one surface to which silicon carbide is present in the pores of the substrate material (continuous from the at least one surface).

20 Preferably, the proportion of elemental silicon deposited on the at least one surface, based on the total weight of the treated substrate, is at most 0.01 wt.%, particularly preferably at most 0.001 wt.%.

25 Preferably, the treated substrate has no residue of elemental silicon particles having a particle diameter of at least 500 μm on the at least one surface. The particle size of the silicon particles can be determined, for example, by laser diffraction (e.g., according to ISO 13320:2020-01).

Particularly preferably, the treated substrate has no residues of elemental silicon (or no elemental silicon) on the at least one surface.

Very preferably, the treated substrate does not contain any residues of elemental silicon (or no elemental silicon).

30 Preferably, the pores of the substrate material in the infiltration zone are not filled (or partially filled) with any substance other than silicon carbide.

Preferably, the pores of the substrate material in the infiltration zone are completely filled with silicon carbide

A preferred embodiment of the treated substrate according to the invention is characterized in that the treated substrate

- 5 - has a permeability of not more than $1 \cdot 10^{-16} \text{ m}^2$, preferably not more than $1 \cdot 10^{-17} \text{ m}^2$, particularly preferably not more than $1 \cdot 10^{-19} \text{ m}^2$, and/or
- has a permeability which is lower by a factor of at least 10, preferably of at least 100, than a (or the) permeability of the substrate before the
- 10 treatment, and/or
- has an open porosity in the infiltration zone, determined by mercury porosimetry, of not more than 8%, preferably not more than 5%, and/or
- has in the infiltration zone an open porosity, determined by mercury
- 15 porosimetry, which is lower by at least 7%, preferably by at least 10%, particularly preferably by at least 12%, relative to the total volume of the treated substrate, than an (or the) open porosity (determined by mercury porosimetry) of the treated substrate outside the infiltration zone, and/or
- 20 - has a resistivity of at most 1500 mΩcm, preferably at most 10 mΩcm, and/or
- does not contain any elemental silicon.

25 The (gas) permeability of the treated substrate and/or the (gas) permeability of the substrate before treatment can, for example, be determined using the differential pressure method (e.g. in accordance with EN 993-4 : 1995).

30 The presence of the feature that the treated substrate has a permeability which is lower by a factor of at least 10, preferably at least 100, than the permeability of the substrate before treatment can, for example, only be determined on the treated substrate by first determining the permeability of the treated substrate, e.g. by means of the differential pressure method (e.g. according to EN 993-4 : 1995), then removing the infiltration zone from the treated substrate, e.g. by grinding it off, then determining the permeability of the substrate thus obtained without the infiltration zone, e.g. by means of the

differential pressure method (e.g. according to EN 993-4 : 1995), and finally comparing the two determined permeabilities with each other or setting them in a corresponding ratio. The permeability of the treated substrate from which the infiltration zone has been removed is the same as the permeability of the untreated substrate.

5

The open porosity in the infiltration zone of the treated substrate and the open porosity of the treated substrate outside the infiltration zone are determined by mercury porosimetry (e.g. according to DIN 66133:1993-06).

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The open porosity of the treated substrate outside the infiltration zone corresponds to the open porosity of the untreated substrate (also in the area of the later infiltration zone).

A further preferred embodiment of the treated substrate according to the invention is characterized in that

15

- the infiltration zone has an average thickness of at least 100 μm , preferably from 100 μm to 1200 μm , particularly preferably from 200 μm to 800 μm , and/or
- the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled contains 3C-SiC (3C-silicon carbide), preferably having 3C-SiC (3C-silicon carbide) as the

20

main phase.

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The (mean) thickness of the infiltration zone can also be referred to as the (mean) infiltration depth. In other words, the average infiltration depth is preferably in a range of at least 100 μm , preferably from 100 μm to 1200 μm , particularly preferably from 200 μm to 800 μm . The thickness of the infiltration zone or the depth of infiltration extends from the treated surface to the edge of the infiltration zone opposite the treated surface.

30

The average thickness of the infiltration zone or the average infiltration depth can be determined, for example, by determining individual measured values for the thickness of the infiltration zone or the infiltration depth at various points distributed over the entire length and/or width of the infiltration zone by means of optical microscopy on transverse sections (vertical to the direction of infiltration) and then calculating an average value of the individual

measured values. Here, the thickness of the infiltration zone or the infiltration depth can be averaged over the entire length and/or width of the infiltration zone.

5 The average thickness of the infiltration zone or the average infiltration depth can be determined, for example, according to DIN EN ISO 1463:2021-08.

X-ray diffraction (XRD) can be used to determine that the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled contains 3C-SiC.

10 Preferably, the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled has 3C-SiC (3C silicon carbide) as the main phase.

15 The fact that the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled comprises 3C-SiC as the main phase means that the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled, comprises a 3C silicon carbide phase and does not comprise any other phases having a higher weight percentage of the total silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled than the 3C silicon carbide phase.

20 X-ray diffraction (XRD) can be used to determine that the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled has 3C-SiC as the main phase.

3C-SiC (3C silicon carbide) may also be referred to as β -SiC (β -silicon carbide).

25 Preferably, the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled has a content of at least 50% by weight, preferably a content of at least 70% by weight, more preferably a content of at least 90% by weight, very particularly preferably a content of at least 95% by weight, for example a content of at least 99% by weight, 3C-SiC (3C silicon carbide) or β -SiC (β -silicon carbide).

30 Preferably, the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled has a content of at most 5%

by weight, preferably a content of at most 1% by weight, particularly preferably a content of at most 0.1% by weight, of α -SiC (α -silicon carbide). Particularly preferably, the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled does not contain α -SiC (α -silicon carbide).

The proportion of 3C-SiC or β -SiC and/or the proportion of α -SiC in the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled can be determined by means of X-ray diffraction (XRD), for example.

A very particularly preferred embodiment of the substrate according to the invention is characterized in that the infiltration zone has an average thickness of at least 100 μm (e.g. 100 μm to 1200 μm), preferably of at least 200 μm (e.g. 200 μm to 800 μm), and the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled contains β -SiC (or 3C-SiC), preferably having β -SiC (or 3C-SiC) as the main phase.

The fact that the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled has β -SiC (or 3C-SiC) as the main phase can be determined, for example, by means of X-ray diffraction (XRD).

Another preferred embodiment of the treated substrate of the invention is characterized in that the carbon-containing (or carbonaceous) material is selected from the group consisting of graphite, preferably iso-graphite; carbon fiber reinforced carbon; silicon carbide fiber reinforced carbon; silicon carbide fiber reinforced silicon carbide; sintered silicon carbide; glassy carbon; and combinations thereof.

A further preferred embodiment of the treated substrate according to the invention is characterized in that the silicon carbide is doped with at least one dopant selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorus (P), vanadium (V), scandium (Sc), gallium (Ga), indium (In), germanium (Ge), tin (Sn), lead (Pb), arsenic (As), antimony (Sb), bismuth (Bi), and mixtures thereof, wherein the at least one dopant is preferably

- selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorus (P), vanadium (V), scandium (Sc), and mixtures thereof, and/or
- is present in the infiltration zone in a concentration in the range from $1 \cdot 10^{10}$ atoms per cm^3 to $1 \cdot 10^{23}$ atoms per cm^3 , preferably in the range from $1 \cdot 10^{12}$ atoms per cm^3 to $1 \cdot 10^{21}$ atoms per cm^3 , particularly preferably in the range from $1 \cdot 10^{15}$ atoms per cm^3 to $1 \cdot 10^{18}$ atoms per cm^3 .

By the incorporation of one or more dopants or dopant elements into the (e.g. polycrystalline) silicon carbide, the electrical and/or thermal properties of the treated substrate can be varied or specifically adjusted. Material characteristics that can be adjusted with this are, for example, the (specific) resistance, the electrical conductivity and the thermal conductivity of the silicon carbide. Depending on selection and concentration of the respective dopant element, electrical and thermal properties can also be adjusted independently of each other.

Preferably, the at least one dopant can be at least one p-type dopant, which is particularly preferably selected from the group consisting of aluminum (Al), boron (B), vanadium (V), scandium (Sc), gallium (Ga), indium (In), and mixtures thereof, wherein the at least one p-type dopant is particularly preferably selected from the group consisting of aluminum (Al), boron (B), vanadium (V), scandium (Sc), and mixtures thereof.

A further preferred embodiment of the treated substrate according to the invention is characterized in that the treated substrate

- has the infiltration zone, in which the pores of the substrate material are at least partially filled with silicon carbide, at each surface (or over the entire surface of the substrate), and/or
- has an oxidation resistance characterized in that, after exposure of the treated substrate in synthetic air (200 ml/min, 1 bar) for at least 100 h, preferably for at least 150 h, particularly preferably for at least 162 h, at 1100 °C, a mass decrease of the treated substrate (compared with the treated substrate before the exposure in synthetic air) is less than

$1 \cdot 10^{-4} \text{ g/cm}^2$, preferably less than $2,5 \cdot 10^{-5} \text{ g/cm}^2$ (in relation to the entire surface of the treated substrate).

5 A further preferred embodiment of the treated substrate according to the invention is characterized in that the treated substrate is producible or produced by the method according to the invention.

Another preferred embodiment of the treated substrate according to the invention is characterized in that at least one protective layer comprising at least one refractory metal carbide (e.g. tantalum carbide) is disposed on the at least one surface on which the substrate has an infiltration zone.
10 Preferably, the at least one protective layer is a refractory metal carbide layer (e.g., a tantalum carbide layer).

The present invention further relates to the use of the treated substrate according to the invention as a component for high temperature furnaces, preferably heater, insulation component, support; as crucible or crucible
15 element.

The present invention also relates to the following aspects:

20 Aspect 1

A method for treating porous substrates, in which

- a) at least one surface of a porous carbon-containing (or carbonaceous) substrate is provided with at least one silicon coating by applying at least one aqueous suspension comprising silicon particles, at least one binding
25 agent and water to the at least one surface and thereafter subjecting it to a drying process, and
- b) the at least one silicon coating is subjected to at least one heat treatment in which the silicon coating melts into a melt which infiltrates into pores of the porous carbon-containing (or carbonaceous) substrate, silicon
30 contained in the melt being at least partially converted into silicon carbide.

Aspect 2

5 The method according to the preceding aspect, characterized in that the silicon particles have an average particle size in the range from 10 μm to 3500 μm , preferably from 310 μm to 1700 μm , particularly preferably from 500 to 1000 μm .

Aspect 3

10 The method according to any one of the preceding aspects, characterized in that the at least one binding agent

- ensures an adhesive strength of the silicon coating of at least 0.15 MPa, and/or
- is selected from the group consisting of polyvinyl alcohol, polyethylene glycol, polyvinyl butyral, polyacrylic acid, polyurethane, chloroprene rubber, phenolic resin, acrylic resin, cellulose, cellulose derivatives, 15 alginic acid, dextrin, and mixtures thereof.

Aspect 4

20 The method according to any one of the preceding aspects, characterized in that the at least one aqueous suspension

- contains 1 to 50% by weight, preferably 5 to 35% by weight, of the silicon particles, based on the total weight of the at least one aqueous suspension, and/or
- contains 0.01 to 3% by weight, preferably 0.05 to 0.3% by weight, of 25 the at least one binding agent, based on the total weight of the at least one aqueous suspension.

Aspect 5

30 The method according to any one of the preceding aspects, characterized in that the application of the at least one aqueous suspension in step a) takes

place by means of dipping, brushing, doctoring, and/or spray application, preferably by means of spray application.

Aspect 6

- 5 The method according to any one of the preceding aspects, characterized in that the drying process is carried out at a temperature in the range from 10 °C to 200 °C, preferably from 80 °C to 100 °C, and/or for a duration of from 5 h to 48 h, preferably from 10 h to 12 h.

10 Aspect 7

The method according to any one of the preceding aspects, characterized in that the at least one heat treatment

- takes place at a temperature in the range from 1400 °C to 1800 °C, preferably from 1450 °C to 1550 °C, and/or
- 15 - takes place over a period of 1 h to 10 h, preferably 4 h to 6 h, and/or
- takes place under vacuum or under inert gas atmosphere, preferably argon atmosphere, at a (process) pressure of from 10 mbar to 2000 mbar, preferably from 100 mbar to 1800 mbar, more preferably from 500 mbar to 1500 mbar, most preferably from 800 mbar to 1200 mbar.

20

Aspect 8

The method according to any one of the preceding aspects, characterized in that

- the porous carbon-containing (or carbonaceous) substrate comprises or consists of a material selected from the group consisting of
- 25 graphite, preferably iso-graphite; carbon fiber reinforced carbon; silicon carbide fiber reinforced carbon; silicon carbide fiber reinforced silicon carbide; glassy carbon; sintered silicon carbide; silicon infiltrated silicon carbide; and combinations thereof, and/or
- 30 - the porous carbon-containing (or carbonaceous) substrate comprises or consists of a material having a coefficient of thermal expansion of at

least $2.8 \cdot 10^{-6} \text{ K}^{-1}$, preferably of at least $3.0 \cdot 10^{-6} \text{ K}^{-1}$, more preferably of at least $3.2 \cdot 10^{-6} \text{ K}^{-1}$, and/or

- the porous carbon-containing (or carbonaceous) substrate has an open porosity, measured by mercury porosimetry, of at least 12%, preferably from 12% to 30%, more preferably from 14% to 25%, most preferably from 15% to 20%, and/or
- the pores of the porous carbon-containing (or carbonaceous) substrate have an average pore diameter in the range from 0.1 μm to 10 μm , preferably from 1 μm to 5 μm , particularly preferably from 1.5 μm to 5 μm .

Aspect 9

The method according to any one of the preceding aspects, characterized in that the infiltration depth of the melt is adjusted by the amount per unit area of the at least one aqueous suspension applied to the at least one surface and/or by the pressure during the at least one heat treatment.

Aspect 10

A treated substrate comprising a carbon-containing (or carbonaceous) substrate material having pores, the substrate having on at least one surface an infiltration zone in which the pores of the substrate material are at least partially filled with silicon carbide, wherein the treated substrate has a permeability of at most $5 \cdot 10^{-15} \text{ m}^2$ and wherein the treated substrate has an open porosity in the infiltration zone, determined by mercury porosimetry, of at most 10%.

Aspect 11

The treated substrate according to aspect 10, characterized in that the treated substrate

- has a permeability of not more than $1 \cdot 10^{-16} \text{ m}^2$, preferably not more than $1 \cdot 10^{-17} \text{ m}^2$, particularly preferably not more than $1 \cdot 10^{-19} \text{ m}^2$, and/or
- has a permeability which is lower by a factor of at least 10, preferably at least 100, than a permeability of the substrate before the treatment, and/or
- has an open porosity in the infiltration zone, determined by mercury porosimetry, of not more than 8%, preferably not more than 5%, and/or
- has an open porosity in the infiltration zone, determined by mercury porosimetry, which is lower by at least 7%, preferably by at least 10%, particularly preferably by at least 12%, relative to the total volume of the treated substrate, than an open porosity of the treated substrate outside the infiltration zone, and/or
- has a resistivity of at most 1500 mΩcm, preferably at most 10 mΩcm, and/or
- does not contain any elemental silicon.

Aspect 12

- The treated substrate according to aspect 10 or 11, characterized in that
- the infiltration zone has an average thickness of at least 100 μm, preferably from 100 μm to 1200 μm, particularly preferably from 200 μm to 800 μm, and/or
 - the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled contains 3C-SiC, preferably has 3C-SiC as the main phase.

Aspect 13

- The treated substrate according to any one of aspects 10 to 12, characterized in that the carbon-containing (or carbonaceous) material is selected from the group consisting of graphite, preferably iso-graphite; carbon fiber reinforced carbon; silicon carbide fiber reinforced carbon; silicon carbide fiber reinforced

silicon carbide; sintered silicon carbide; glassy carbon; and combinations thereof.

Aspect 14

- 5 The treated substrate according to any one of aspects 10 to 13, characterized in that it is preparable or is prepared using a method according to any one of aspects 1 to 9.

Aspect 15

- 10 A use of a treated substrate according to any one of claims 10 to 14 as a component for high temperature furnaces, preferably heater, insulation component, support; as crucible or crucible element.

- 15 The present invention will be explained in more detail with reference to the following Figures and examples without restricting the invention to the specifically shown parameters.

Embodiment example 1

- 20 Four different porous graphite substrates are provided, each differing from each other in mean pore diameter. The pores of graphite substrate 1A have an average pore diameter of 0.6 μm , the pores of graphite substrate 1B have an average pore diameter of 1.5 μm , the pores of graphite substrate 1C have an average pore diameter of 1.8 μm , and the pores of graphite substrate 1D
- 25 have an average pore diameter of 2.2 μm .

The porous graphite substrates have a substrate geometry of 5x5x1 cm^3 .

a) Preparation of the suspension

A suspension with the following composition is prepared:

- 66.7 wt.% H₂O dist.
- 0.3 wt.% binding agent (e.g. Peptapon 520, powdered solid, Zschimmer & Schwarz Chemie GmbH)
- 33 wt% silicon granules (Si fracture, d50 approx. 800 µm)

5 First, the distilled water (H₂O dist.) and the binding agent are weighed and placed in a vessel. For homogenization and dissolution of the binding agent, the suspension is aged for 20 h on roller stand at 30 rpm (vessel). The silicon granules are then weighed out and added to the suspension. To homogenize the suspension with solid content, it is aged for 15 min on a roller stand at 30 rpm (vessel).

b) Coating process

The coating is applied by spray application. The suspension is atomized by means of compressed air (4 bar). The suspension is fed by means of a nozzle (diameter 2.5 mm). The substrates are each mounted with the area to be coated (5x5 cm²) perpendicular to the nozzle and thus to the direction of the spray jet, with the respective substrate being rotated at 10 rpm. The distance from nozzle to substrate surface is 20 cm. Coating is carried out for all substrates with a spray time of 8 s. A constant application of 0.06 ± 0.015 g suspension/cm² or 0.02 ± 0.005 g Si/cm² is applied.

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c) Drying process

The coated substrates are removed to the oven for drying for 20 h at 90 °C in air.

d) Infiltration process

25 The dried substrates are placed in graphitic sample chamber in an oven. The coated surfaces have no contact with the furnace internals. The furnace volume is evacuated (10^{-3} mbar) and heated up at 250 K/h from room temperature to 1500°C. The temperature of 1500 °C is maintained for 5 h. This is followed by cooling from 1500 °C to room temperature at 200 K/h

30 (cooling rate decreases from 700 °C to as low as 50 K/min because there is no

active cooling) After cooling, the furnace volume is flooded with argon up to atmospheric pressure and the substrates are removed.

5 The treated substrates obtained in this way all show no residues of elemental silicon on the respective treated surface and are thus all characterized by a very high surface quality.

10 The permeability of the treated substrates was determined using the differential pressure method (e.g. according to EN 993-4 : 1995). In the diagram in Fig. 1, the permeability of the treated substrates is compared with the permeability of the untreated starting substrates. As can be seen well, the permeability of the substrates could be significantly reduced by treatment with the method according to the invention. Each of the treated substrates has a permeability of less than $5 \cdot 10^{-15} \text{ m}^2$. In addition, the treated substrates have an open porosity, determined by mercury porosimetry, of no more than 10% in the infiltration zone.

15 From the low permeability and low open porosity of the treated substrates, it can be concluded that for each of the treated substrates, the near-surface pores are nearly or substantially completely closed, and thus the respective treated surface is nearly or substantially completely sealed, so that all substrates are very well protected from penetration of corrosive gases or
20 fluids into the material. Since the treated substrate obtained by treating graphite substrate 1B has the lowest permeability, this treated substrate has the best sealing of the treated surface.

Embodiment example 2

25 Several porous iso-graphite substrates (substrates of isostatically pressed graphite) of four different iso-graphite types are provided. The iso-graphite type 2A substrates have a porosity of 15% and pores with an average pore diameter of $2.2 \text{ }\mu\text{m}$. The iso-graphite type 2B substrates have a porosity of 14% and pores with an average pore diameter of $1.5 \text{ }\mu\text{m}$. The iso-graphite
30 type 2C substrates have a porosity of 10% and pores with an average pore diameter of $1.8 \text{ }\mu\text{m}$. The iso-graphite type 2D substrates have a porosity of 10% and pores with an average pore diameter of $0.6 \text{ }\mu\text{m}$.

The porous graphite substrates have a substrate geometry of 5x5x1 cm³.

a) Preparation of the suspension

A suspension with the following composition is prepared:

- 66.7 wt.% H₂O dist.
- 5 - 0.3 wt.% binding agent (e.g. Peptapon 520, powdered solid, Zschimmer & Schwarz Chemie GmbH)
- 33 wt% silicon granules (Si fracture, d50 approx. 800 µm)

10 First, the distilled water (H₂O dist.) and the binding agent are weighed and placed in a vessel. For homogenization and dissolution of the binding agent, the suspension is aged for 20 h on roller stand at 30 rpm (vessel). The silicon granules are then weighed out and added to the suspension. To homogenize the suspension with solid content, it is aged for 15 min on a roller stand at 30 rpm (vessel).

b) Coating process

15 The coating is applied by spray application. The suspension is atomized by means of compressed air (4 bar). The suspension is fed by means of a nozzle (diameter 2.5 mm). The substrates are each mounted with the area to be coated (5x5 cm²) perpendicular to the nozzle and thus to the direction of the spray jet, with the respective substrate being rotated at 10 rpm. The distance from nozzle to substrate surface is 20 cm. The coating is applied with different spray times of 4 s, 8 s, 12 s, 16 s, 20 s and 24 s, depending on the quantity to be applied. An application per 4 s of approx. 0.01 ± 0.005 g Si/cm² is carried out. After each coating cycle of 4 s, the samples are intermediately dried on a hot plate in air at 100 °C for 15 min.

25 Different amounts of silicon per unit area are applied to the substrates of the four different iso-graphite types. Six substrates of iso-graphite type 2A are subjected to a coating process, the silicon amounts used per unit area being 0.008 g/cm², 0.018 g/cm², 0.033 g/cm², 0.044 g/cm², 0.055 g/cm² and 0.076 g/cm². Six substrates of iso-graphite type 2B are also subjected to a coating process, with the silicon amounts used per unit area being 0.007 g/cm², 0.022 g/cm², 0.028 g/cm², 0.038 g/cm², 0.056 g/cm² and 0.072 g/cm². Four

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substrates of iso-graphite type 2C are subjected to a coating process, the silicon amounts used per unit area being 0.011 g/cm², 0.02 g/cm², 0.03 g/cm² and 0.045 g/cm². Finally, three substrates of iso-graphite type 2D are subjected to a coating process, with the silicon amounts used per unit area being 0.008 g/cm², 0.02 g/cm² and 0.025 g/cm².

c) Drying process

The coated substrates are removed to the oven for drying for 20 h at 90 °C in air.

d) Infiltration process

The dried substrates are placed in graphitic sample chamber in an oven. The coated surfaces have no contact with the furnace internals. The furnace volume is evacuated (10^{-3} mbar) and heated up at 250 K/h from room temperature to 1500°C. The temperature of 1500 °C is maintained for 5 h. This is followed by cooling from 1500 °C to room temperature at 200 K/h (cooling rate decreases from 700 °C to as low as 50 K/min because there is no active cooling) After cooling, the furnace volume is flooded with argon up to atmospheric pressure and the substrates are removed.

The treated substrates obtained in this way all show no residues of elemental silicon on the respective treated surface and are thus all characterized by a very high surface quality.

The permeability of the treated substrates was determined using the differential pressure method (e.g. according to EN 993-4 : 1995). In the diagram in Fig. 2, the determined values for the permeability of the respective treated substrates are shown graphically. In addition, the permeability of an untreated starting substrate of each of the four iso-graphite types is also plotted in the diagram. As can be seen well, the permeability of the substrates could be significantly reduced by treatment with the method according to the invention. Each of the treated substrates has a permeability $\leq 5 \cdot 10^{-15}$ m². In addition, the treated substrates have an open porosity, determined by mercury porosimetry, of no more than 10% in the infiltration zone.

From Fig. 2 it can be seen that the permeability decreases with an increase of the applied silicon amount, whereas for graphite substrate 2D already an applied silicon amount of 0.025 gSi/cm^2 is sufficient to obtain a permeability $\leq 1 \cdot 10^{-19} \text{ m}^2$ and thus below the measurement limit. The higher the initial permeability of the untreated substrate, the more silicon must be infiltrated to obtain a permeability $\leq 1 \cdot 10^{-19} \text{ m}^2$ and thus below the measurement limit.

From the low permeability and low open porosity of the treated substrates, it can be concluded that for each of the treated substrates, the near-surface pores are nearly or substantially completely closed, and thus the respective treated surface is nearly or substantially completely sealed, so that all substrates are very well protected from penetration of corrosive gases or fluids into the material.

By varying the amount of Si applied, the permeability or open porosity of the substrate can be varied and adjusted accordingly for the application.

Embodiment example 3

Several porous iso-graphite substrates (substrates of isostatically pressed graphite) of four different iso-graphite types are provided. The iso-graphite type 3A substrates have a porosity of 15% and pores with an average pore diameter of $2.2 \text{ }\mu\text{m}$. The iso-graphite type 3B substrates have a porosity of 14% and pores with an average pore diameter of $1.5 \text{ }\mu\text{m}$. The iso-graphite type 3C substrates have a porosity of 10% and pores with an average pore diameter of $1.8 \text{ }\mu\text{m}$. The iso-graphite type 3D substrates have a porosity of 10% and pores with an average pore diameter of less than $0.6 \text{ }\mu\text{m}$.

The porous graphite substrates have a substrate geometry of $5 \times 5 \times 1 \text{ cm}^3$.

a) Preparation of the suspension

A suspension with the following composition is prepared:

- 66.7 wt.% H_2O dist.
- 0.3 wt.% binding agent (e.g. Peptapon 520, powdered solid, Zschimmer & Schwarz Chemie GmbH)

- 33 wt% silicon granules (Si fracture, d50 approx. 800 μm)

5 First, the distilled water (H_2O dist.) and the binding agent are weighed and placed in a vessel. For homogenization and dissolution of the binding agent, the suspension is aged for 20 h on roller stand at 30 rpm (vessel). The silicon granules are then weighed out and added to the suspension. To homogenize the suspension with solid content, it is aged for 15 min on a roller stand at 30 rpm (vessel).

b) Coating process

10 The coating is applied by spray application. The suspension is atomized by means of compressed air (4 bar). The suspension is fed by means of a nozzle (diameter 2.5 mm). The substrates are each mounted with the area to be coated ($5 \times 5 \text{ cm}^2$) perpendicular to the nozzle and thus to the direction of the spray jet, with the respective substrate being rotated at 10 rpm. The distance from nozzle to substrate surface is 20 cm. The coating is applied with different
15 spray times of 4 s, 8 s, 12 s, 16 s, 20 s and 24 s, depending on the quantity to be applied. An application per 4 s of approx. $0.01 \pm 0.005 \text{ g Si/cm}^2$ is carried out. After each coating cycle of 4 s, the samples are intermediately dried on a hot plate in air at 100°C for 15 min.

20 Different amounts of silicon per unit area are applied to the substrates of the four different iso-graphite types. Four substrates of iso-graphite type 3A are subjected to a treatment according to the invention, the amounts of silicon used per unit area being 0.008 g/cm^2 , 0.018 g/cm^2 , 0.033 g/cm^2 and 0.044 g/cm^2 . Four substrates of iso-graphite type 3B are also subjected to a treatment according to the invention, the amounts of silicon used per unit
25 area being 0.007 g/cm^2 , 0.022 g/cm^2 , 0.038 g/cm^2 and 0.056 g/cm^2 . Four substrates of iso-graphite type 3C are also subjected to a treatment according to the invention, the amounts of silicon used per unit area being 0.011 g/cm^2 , 0.02 g/cm^2 , 0.03 g/cm^2 and 0.045 g/cm^2 . Finally, three substrates of the iso-graphite type 3D are subjected to a treatment according to the invention, the
30 amounts of silicon used per unit area being 0.02 g/cm^2 , 0.025 g/cm^2 and 0.035 g/cm^2 .

c) Drying process

The coated substrates are removed to the oven for drying for 20 h at 90 °C in air.

d) Infiltration process

5 The dried substrates are placed in graphitic sample chamber in an oven. The coated surfaces have no contact with the furnace internals. The furnace volume is evacuated (10^{-3} mbar) and heated up at 250 K/h from room temperature to 1500°C. The temperature of 1500 °C is maintained for 5 h. This is followed by cooling from 1500 °C to room temperature at 200 K/h (cooling rate decreases from 700 °C to as low as 50 K/min because there is no
10 active cooling) After cooling, the furnace volume is flooded with argon up to atmospheric pressure and the substrates are removed.

The treated substrates obtained in this way all show no residues of elemental silicon on the respective treated surface and are thus all characterized by a very high surface quality.

15 The permeability of the treated substrates was determined using the differential pressure method (e.g. according to EN 993-4 : 1995). In the diagram in Fig. 3, the determined values for the permeability of the respective treated substrates are shown graphically. Each of the treated substrates has a permeability $\leq 5 \cdot 10^{-15}$ m². In addition, the treated substrates have an open
20 porosity, determined by mercury porosimetry, of no more than 10% in the infiltration zone.

The mean infiltration depth (or mean thickness of the infiltration zone) was determined by optical microscopy on cross-sections vertical to the direction of infiltration and averaged over the entire sample length (5 cm).

25 The diagram in Fig. 3 shows that the permeability of the infiltrated substrate basically decreases with the infiltration depth (or the thickness of the infiltration zone). The decrease over the infiltration depth becomes more pronounced as the initial permeability of the untreated graphite material decreases. The permeability can thus be adjusted by the infiltration depth of
30 the graphite material and thus by the amount of Si applied.

Embodiment example 4

Six substrates of iso-graphite type 4A are provided. These have a porosity of 10% and pores with an average pore diameter of 1.8 μm .

The porous graphite substrates have a substrate geometry of 5x5x1 cm^3 .

5 a) Preparation of the suspension

A suspension with the following composition is prepared:

- 66.7 wt.% H_2O dist.
- 0.3 wt.% binding agent (e.g. Peptapon 520, powdered solid, Zschimmer & Schwarz Chemie GmbH)
- 10 - 33 wt% silicon granules (Si fracture, d50 approx. 800 μm)

First, the distilled water (H_2O dist.) and the binding agent are weighed and placed in a vessel. For homogenization and dissolution of the binding agent, the suspension is aged for 20 h on roller stand at 30 rpm (vessel). The silicon granules are then weighed out and added to the suspension. To homogenize the suspension with solid content, it is aged for 15 min on a roller stand at 30 rpm (vessel).

15 b) Coating process

The coating is applied by spray application. The suspension is atomized by means of compressed air (4 bar). The suspension is fed by means of a nozzle (diameter 2.5 mm). The substrates are each mounted with the area to be coated (5x5 cm^2) perpendicular to the nozzle and thus to the direction of the spray jet, with the respective substrate being rotated at 10 rpm. The distance from nozzle to substrate surface is 20 cm. The coating is applied with different spray times of 8 s and 12 s depending on the quantity to be applied. An application per 4 s of approx. $0.01 \pm 0.005 \text{ g Si/cm}^2$ is carried out. After each coating cycle of 4 s, the samples are intermediately dried on a hot plate in air at 100 $^\circ\text{C}$ for 15 min.

Different amounts of silicon per unit area are applied to the six iso-graphite type 4A substrates, the amount of silicon per unit area used being $0.02 \pm$

0.005 g/cm² for three of the six substrates and 0.03 ± 0.005 g/cm² for the other three of the six substrates.

c) Drying process

5 The coated substrates are removed to the oven for drying for 20 h at 90 °C in air.

d) Infiltration process

The dried substrates are subjected to different infiltration processes with different process conditions.

10 In this process, all dried substrates are placed in graphitic sample chambers in an oven, with the coated surfaces not in contact with the oven internals. For all substrates, evacuation of the furnace volume takes place (10^{-3} mbar).

15 For the first of the substrates infiltrated with a silicon amount of 0.02 ± 0.005 g/cm² and for the first of the substrates infiltrated with a silicon amount of 0.03 ± 0.005 g/cm², the vacuum is maintained throughout the rest of the process. For the second of the substrates infiltrated with a silicon amount of 0.02 ± 0.005 g/cm², and for the second of the substrates infiltrated with a silicon amount of 0.03 ± 0.005 g/cm², argon is instead flooded and a pressure of 20 mbar is maintained throughout the rest of the process. Finally, for the third of the substrates infiltrated with a silicon amount of 0.02 ± 0.005 g/cm² and for the third of the substrates infiltrated with a silicon amount of 0.03 ± 0.005 g/cm², argon is flooded and a pressure of 1000 mbar is maintained throughout the rest of the process.

20

25 This is followed by heating at 250 K/h from room temperature to 1500 °C for all substrates, with the temperature of 1500 °C being maintained for 5 h. This is followed by cooling from 1500 °C to room temperature at 200 K/h for all substrates (cooling rate decreases from 700 °C to as low as 50 K/min due to lack of active cooling) After cooling, the furnace volume is flooded with argon up to atmospheric pressure and the substrates are removed.

30 The mean infiltration depth (or mean thickness of the infiltration zone) was determined by optical microscopy on cross-sections vertical to the direction of infiltration and averaged over the entire sample length (5 cm).

The mean infiltration depths of the treated substrates determined in each case are shown in the diagram in Fig. 4 as a function of the applied silicon quantity.

5 It can be seen that the Si infiltration depth can be adjusted by the process pressure. If the infiltration process is run under vacuum, an infiltration depth between 325 and 350 μm can be set for a Si quantity of $0.02 \pm 0.005 \text{ g/cm}^2$ to $0.03 \pm 0.005 \text{ g/cm}^2$. If an argon pressure of 20 mbar is set for the infiltration process, a decrease in infiltration depth to 275 μm or 290 μm can be observed. If the process pressure is further increased to 1000 mbar, a
10 significant increase in infiltration depth to 375 μm or 400 μm can be achieved.

Consequently, by varying the process pressure, the depth of the infiltration zone can be influenced and adjusted.

Embodiment example 5

15 Two substrates of iso-graphite type 5A are provided. This has pores with an average pore diameter of 1.8 μm .

One of the two substrates is used for the determination of permeability after infiltration and has a substrate geometry of $5 \times 5 \times 1 \text{ cm}^3$. The other of the two substrates is used for the determination of open porosity in the infiltration
20 zone after infiltration and has a substrate geometry of $2 \times 0.5 \times 0.5 \text{ cm}^3$

a) Preparation of the suspension

A suspension with the following composition is prepared:

- 66.7 wt.% H_2O dist.
- 0.3 wt.% binding agent (e.g. Peptapon 520, powdered solid,
25 Zschimmer & Schwarz Chemie GmbH)
- 33 wt% silicon granules (Si fracture, d50 approx. 800 μm)

First, the distilled water (H_2O dist.) and the binding agent are weighed and placed in a vessel. For homogenization and dissolution of the binding agent, the suspension is aged for 20 h on roller stand at 30 rpm (vessel). The silicon

granules are then weighed out and added to the suspension. To homogenize the suspension with solid content, it is aged for 15 min on a roller stand at 30 rpm (vessel).

b) Coating process

5 The two substrates are subjected to different coating processes.

Substrate for the determination of permeability:

10 The coating is applied by spray application. The suspension is atomized by means of compressed air (4 bar). The suspension is fed by means of a nozzle (diameter 2.5 mm). The substrates are each mounted with the area to be coated (5x5 cm²) perpendicular to the nozzle and thus to the direction of the spray jet, with the respective substrate being rotated at 10 rpm. The distance from nozzle to substrate surface is 20 cm. The coating is applied with a spraying time of 20 s depending on the quantity to be applied. An application per 4 s of approx. 0.01 ± 0.005 g Si/cm² is carried out. After each coating cycle of 4 s, the samples are intermediately dried on a hot plate in air at 100 °C for 15 min. The total amount of silicon used per unit area is 0.05 ± 0.005 g/cm².

Substrate for the determination of open porosity:

20 The coating is applied to all surfaces of the substrate. Due to the small sample dimensions, the coating could not be applied by spraying. For each area of the graphite sample, the required amount of suspension is weighed to achieve 0.05 ± 0.005 gSi/cm². The weighed suspension quantity is applied to the corresponding surface and distributed evenly by hand with a spatula.

25 Intermediate drying takes place on a hot plate in air at 100 °C for 15 min. The process is then repeated until all surfaces of the specimens are coated with Si.

c) Drying process

The coated substrates are removed to the oven for drying for 20 h at 90 °C in air.

d) Infiltration process

5 The dried substrates are placed in graphitic sample chamber in an oven. The coated surfaces have no contact with the furnace internals. The furnace volume is evacuated (10^{-3} mbar) and heated up at 250 K/h from room temperature to 1500°C. The temperature of 1500 °C is maintained for 5 h. This is followed by cooling from 1500 °C to room temperature at 200 K/h (cooling rate decreases from 700 °C to as low as 50 K/min because there is no active cooling) After cooling, the furnace volume is flooded with argon up to atmospheric pressure and the substrates are removed.

10 The permeability of both the untreated substrate and the treated substrate was determined using the differential pressure method (e.g. in accordance with EN 993-4 : 1995) and the open porosity using mercury porosimetry (e.g. in accordance with DIN 66133:1993-06). In the diagram in Fig. 5a, the determined values for permeability and open porosity are shown graphically.

15 The mercury porosity measurements on the iso-graphene type 5A substrates show that with the infiltration of Si, a significant reduction in porosity from about 17.5% in the initial state to about 6% is achieved. The infiltration of the Si melt leads to the most extensive filling of the pore structures in the graphite material. The images of the microstructure without and with Si
20 infiltration shown in Fig. 5b clearly show that after infiltration only very small pore structures remain unoccluded. Thus, analogous to porosity, the gas permeability of the substrate can also be reduced up to the measurement limit of permeability ($1 \cdot 10^{-19}$ m²).

25 **Embodiment example 6**

In order to investigate the influence of the particle size on the quality of the surface and the infiltration zone of the treated substrate, tests were carried out in which the particle size of the used silicon particles has been varied in a targeted manner.

The remaining framework conditions, such as coating application, substrate material, Si concentration per area, process duration and time, temperature profile, process pressure and atmosphere were kept constant.

a) Preparation of the suspension

5 Two suspensions with the following compositions are prepared:

1st suspension:

- 66.7 wt.% H₂O dist.
- 0.3 wt.% binding agent (e.g. Peptapon 520, powdered solid, Zschimmer & Schwarz Chemie GmbH)
- 10 - 33 wt% silicon granules (Si fracture, d₅₀ approx. 5 µm, max. 20 µm)

2nd suspension:

- 66.7 wt.% H₂O dist.
- 0.3 wt.% binding agent (e.g. Peptapon 520, powdered solid, Zschimmer & Schwarz Chemie GmbH)
- 15 - 33 wt% silicon granules (Si fracture, d₅₀ approx. 800 µm, max. 1600 µm)

20 First, the distilled water (H₂O dist.) and the binding agent are weighed and placed in a vessel. For homogenization and dissolution of the binding agent, the suspension is aged for 20 h on roller stand at 30 rpm (vessel). The silicon powder or silicon granules are then weighed out and added to the suspension. To homogenize the suspension with solid content, it is aged for 15 min on a roller stand at 30 rpm (vessel).

b) Coating process

25 With each of the two suspensions, a graphite substrate with a substrate geometry of 5x5x1 cm³ is coated respectively.

The coating is applied by spray application. The suspension is atomized by means of compressed air (4 bar). The suspension is fed by means of a nozzle (diameter 2.5 mm). The substrates are each mounted with the area to be coated (5x5 cm²) perpendicular to the nozzle and thus to the direction of the

spray jet, with the respective substrate being rotated at 10 rpm. The distance from nozzle to substrate surface is 20 cm. A constant application of approx. $0.07 \pm 0.015 \text{ g Si/cm}^2$ is applied.

c) Drying process

- 5 The coated substrates are removed to the oven for drying for 20 h at 90 °C in air.

d) Infiltration process

The dried substrates are subjected to different infiltration processes with different process conditions.

- 10 The dried substrates are placed in graphitic sample chamber in an oven. The coated surfaces have no contact with the furnace internals. The furnace volume is evacuated (10^{-3} mbar) and heated up at 250 K/h from room temperature to 1500°C. The temperature of 1500 °C is maintained for 5 h. This is followed by cooling from 1500 °C to room temperature at 200 K/h
- 15 (cooling rate decreases from 700 °C to as low as 50 K/min because there is no active cooling). After cooling, the furnace volume is flooded with argon up to atmospheric pressure and the substrates are removed.

Both treated substrates have an open porosity in the infiltration zone, determined by mercury porosimetry, of no more than 10%.

- 20 Fig. 6 shows an overview of the surface of the samples coated with the suspension and the infiltrated samples. For the latter case, vertical cross-sections were also made along the infiltration direction.

- 25 Fig. 6 shows that, in the case of the Si powder (d_{50} approximately 5 μm), isolated silicon carbide crystals are on the surface but these are embedded in a cracked, granular matrix of incompletely molten particles. On the other hand, a highly polycrystalline, crack-free surface can be achieved for the coarser Si granules (d_{50} approximately 800 μm). This makes it fundamentally clear that finer Si material tends to have a lower ability to complete melting. A decisive aspect here is the high specific surface which typically increases
- 30 with the decrease in particle size. On the one hand, in the case of Si, it comes to an increase oxidation of the surface in air but also in contact with water

during the preparation or processing of the suspension. The resulting silicon oxide layer on the particle surface impairs in the following the formation of a molten phase and thus inhibits the infiltration process. In order to avoid this, the oxide layer can be removed from the powder using chemical (e.g. treatment with hydrofluoric acid HF) or thermal processes. However, this is a complex process and cannot be implemented in the case of a Si-based coating. Furthermore, a high specific surface can react with free carbon from the furnace atmosphere or residues of the carbon-based organic suspension additives (e.g. binders) to form SiC close to the surface before the actual melting. The melting of the particles thus only takes place partially and not completely and cracked and porous structures remain.

As a consequence of these observations, it can therefore be stated that a higher average particle size of the silicon particles leads to a more complete melting of the silicon particles thereby favoring the formation of a highly crystalline, crack- and pore-free surface whereas, with the use silicon particles having a lower average particle size, cracks in the surface occur due to a non-complete melting of the silicon particles.

This can also be confirmed by measuring the (gas) permeability using the differential pressure method (e.g. in accordance with EN 993-4 : 1995). The corresponding measurement results are shown in Fig. 7, wherein the graph therein first shows the values for both samples of the embodiment example, in which an application of approx. 0.07 g Si/cm² has been made, and additional values are given for further samples, in which an application of the second suspension has been made with a different application quantity in each case. In the present case, in the event of infiltration of the fine Si powder (d_{50} approx. 5 μm), a permeability of $5,3 \cdot 10^{-18} \text{ m}^2$ can be determined. The initial permeability of the graphite substrate used has a permeability of $2,5 \cdot 10^{-15} \text{ m}^2$. If, on the other hand, Si granules with an average particle size of 800 μm are used, the permeability of the infiltrated substrate lies below the measuring limit of $1 \cdot 10^{-19} \text{ m}^2$, which corresponds to a complete gas-tight sample. This makes it clear that, with fine Si powder, the permeability of graphite materials can be reduced by means of infiltration but, however, these cannot be adjusted to be completely gas-tight and therefore not resistant to oxidation.

Ultimately, the studies show that significantly more gas-tight and less defective surfaces can be produced by using bigger silicon particles than this is the case with finer Si powder. In the case of fine Si powder, a post-processing may also be necessary due to the formation of macrocracks (see Fig. 6) and the associated poor layer adhesion in order to make the component usable for further processing steps or use.

In addition, the tendency of the silicon powder or silicon granules used to oxidize on contact with water was determined via the release of hydrogen H_2 . According to the reaction $Si + 2 H_2O \rightarrow SiO_2 + 2 H_2$, the water molecule is split during the oxidation of Si. This reaction is further favored with increasing specific surface or decreasing particle size. Fig. 8 shows the measured H_2 concentrations over the resting time. The measurement was carried out using a hydrogen measuring probe at a distance of 1 cm from the surface of the suspension. A hydrogen concentration of $1 \cdot 10^{-4}$ vol% was initially measured for the Si powder. This increased over time and finally reached a concentration of 0.04 vol% after 24 hours. For the Si granules, the value for the entire measurement interval was below the measurement limit ($< 5 \cdot 10^{-5}$ vol%).

Embodiment example 7

To investigate the oxidation behavior of a treated substrate produced with the use of silicon particles having a high average particle size, a corresponding treated substrate was produced and then the permeability and oxidation behavior of the treated substrate produced in this way was investigated.

To produce the treated substrate, a cuboid graphite substrate measuring $5 \times 2.5 \times 1 \text{ cm}^3$ (surface area 40 cm^2) was coated over its entire surface with a silicon coating using a suspension comprising silicon particles having a high average particle size (d_{50} approximately $800 \mu\text{m}$) and then subjected to a heat treatment to melt and infiltrate the silicon and convert the silicon into silicon carbide. The sample was prepared in the following steps:

a) Preparation of the suspension

A suspension with the following composition is prepared:

- 66.7 wt.% H₂O dist.
- 0.3 wt.% binding agent (e.g. Peptapon 520, powdered solid, Zschimmer & Schwarz Chemie GmbH)
- 5 - 33 wt% silicon granules (Si fracture, d₅₀ approx. 800 µm, max. 1600 µm)

First, the distilled water (H₂O dist.) and the binding agent are weighed and placed in a vessel. For homogenization and dissolution of the binding agent, the suspension is aged for 20 h on roller stand at 30 rpm (vessel). The silicon granules are then weighed out and added to the suspension. To homogenize the suspension with solid content, it is aged for 15 min on a roller stand at 30 rpm (vessel).

b) Coating process

A graphite substrate with a substrate geometry of 5x5x1 cm³ is coated with the suspension.

The coating is applied by spray application. The suspension is atomized by means of compressed air (4 bar). The suspension is fed by means of a nozzle (diameter 2.5 mm). The substrate is mounted with the area to be coated perpendicular to the nozzle and thus to the direction of the spray jet, with the respective substrate being rotated at 10 rpm. The distance from nozzle to substrate surface is 20 cm. A constant application of 0.04 ± 0.015 g Si/cm² is applied. After drying, the sample is rotated so that a surface that has not yet been coated points vertically to the spray jet and this is coated in the same way. The process is repeated until all sides are coated.

c) Drying process

The coated substrate is removed to the oven for drying for 20 h at 90 °C in air.

d) Infiltration process

The dried substrate is placed in a graphite sample chamber in an oven. The coated surfaces have no contact with the furnace internals. The furnace volume is evacuated (10^{-3} mbar) and heated up at 250 K/h from room

temperature to 1500°C. The temperature of 1500 °C is maintained for 5 h. This is followed by cooling from 1500 °C to room temperature at 200 K/h (cooling rate decreases from 700 °C to as low as 50 K/min because there is no active cooling). After cooling, the furnace volume is flooded with argon up to atmospheric pressure and the substrate is removed.

The treated substrate has an open porosity in the infiltration zone, determined by mercury porosimetry, of no more than 10%. In addition, a permeability of $\leq 1 \cdot 10^{-19} \text{ m}^2$ can be determined for the treated substrate using the differential pressure method (e.g. in accordance with EN 993-4 : 1995).

To investigate the oxidation behavior, the treated substrate was exposed to synthetic air (200 ml/min, 1 bar) for up to 162 h at 1100 °C and the mass was determined at intervals of 6 and 24 h.

The results of this investigation of the oxidation behavior are summarized in Fig. 9. It becomes clear that no decrease in mass could be detected for the sample produced after up to 162 h within the measurement accuracy ($\pm 0.001 \text{ g}$) or that this was less than $2.5 \cdot 10^{-5} \text{ g/cm}^2$ in relation to the sample surface. A slight increase in mass could even be observed, as oxygen is absorbed through the formation of an oxide layer on the silicon carbide infiltration layer. This investigation is also further proof of the enormous density of the infiltration zone and thus of the surface of the treated substrate.

By the use of silicon particles having a high particle size and the resulting production of an extremely dense surface, the oxidation behavior of such coated components can be significantly improved. This results in an exceptionally high oxidation resistance.

Claims

1. A method for treating porous substrates, in which
 - a) at least one surface of a porous carbon-containing substrate is provided with at least one silicon coating by applying at least one aqueous suspension comprising silicon particles, at least one binding agent and water to the at least one surface and thereafter subjecting it to a drying process, and
 - b) the at least one silicon coating is subjected to at least one heat treatment in which the silicon coating melts into a melt which infiltrates into pores of the porous carbon-containing substrate, silicon contained in the melt being at least partially converted into silicon carbide.
2. The method according to the preceding claim, characterized in that the silicon particles have an average particle size in the range from 10 μm to 3500 μm , preferably from 310 μm to 1700 μm , particularly preferably from 500 to 1000 μm .
3. The method according to any one of the preceding claims, characterized in that the silicon particles have an average particle size of more than 500 μm and up to 3500 μm , preferably in the range from 550 μm to 3500 μm , particularly preferably in the range from 650 μm to 1700 μm , most preferably in the range from 750 μm to 1000 μm .
4. The method according to any one of the preceding claims, characterized in that the at least one binding agent
 - ensures an adhesive strength of the silicon coating of at least 0.15 MPa, and/or
 - is selected from the group consisting of polyvinyl alcohol, polyethylene glycol, polyvinyl butyral, polyacrylic acid, polyurethane, chloroprene rubber, phenolic resin, acrylic resin, cellulose, cellulose derivatives, alginic acid, dextrin, and mixtures thereof.

5. The method according to any one of the preceding claims, characterized in that the at least one aqueous suspension
- contains 1 to 50% by weight, preferably 5 to 35% by weight, of the silicon particles, based on the total weight of the at least one aqueous suspension, and/or
 - contains 0.01 to 3% by weight, preferably 0.05 to 0.3% by weight, of the at least one binding agent, based on the total weight of the at least one aqueous suspension.
6. The method according to any one of the preceding claims, characterized in that the application of the at least one aqueous suspension in step a) takes place by means of dipping, brushing, doctoring, and/or spray application, preferably by means of spray application.
7. The method according to any one of the preceding claims, characterized in that the drying process is carried out at a temperature in the range from 10 °C to 200 °C, preferably from 80 °C to 100 °C, and/or for a duration of from 5 h to 48 h, preferably from 10 h to 12 h.
8. The method according to any one of the preceding claims, characterized in that the at least one heat treatment
- takes place at a temperature in the range from 1400 °C to 1800 °C, preferably from 1450 °C to 1550 °C, and/or
 - takes place over a period of 1 h to 10 h, preferably 4 h to 6 h, and/or
 - takes place under vacuum or under inert gas atmosphere, preferably argon atmosphere, at a (process) pressure of from 10 mbar to 2000 mbar, preferably from 100 mbar to 1800 mbar, more preferably from 500 mbar to 1500 mbar, most preferably from 800 mbar to 1200 mbar.
9. The method according to any one of the preceding claims, characterized in that

- 5

 - the porous carbon-containing substrate comprises or consists of a material selected from the group consisting of graphite, preferably iso-graphite; carbon fiber reinforced carbon; silicon carbide fiber reinforced carbon; silicon carbide fiber reinforced silicon carbide; glassy carbon; sintered silicon carbide; silicon infiltrated silicon carbide; and combinations thereof, and/or
- 10

 - the porous carbon-containing substrate comprises or consists of a material having a coefficient of thermal expansion of at least $2.8 \cdot 10^{-6} \text{ K}^{-1}$, preferably of at least $3.0 \cdot 10^{-6} \text{ K}^{-1}$, more preferably of at least $3.2 \cdot 10^{-6} \text{ K}^{-1}$, and/or
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 - the porous carbon-containing substrate has an open porosity, measured by mercury porosimetry, of at least 12%, preferably from 12% to 30%, more preferably from 14% to 25%, most preferably from 15% to 20%, and/or
- 15

 - the pores of the porous carbon-containing substrate have an average pore diameter in the range from $0.1 \text{ }\mu\text{m}$ to $10 \text{ }\mu\text{m}$, preferably from $1 \text{ }\mu\text{m}$ to $5 \text{ }\mu\text{m}$, particularly preferably from $1.5 \text{ }\mu\text{m}$ to $5 \text{ }\mu\text{m}$.
- 20

10. The method according to any one of the preceding claims, characterized in that the infiltration depth of the melt is adjusted by the amount per unit area of the at least one aqueous suspension applied to the at least one surface and/or by the pressure during the at least one heat treatment.
- 25

11. The method according to any one of the preceding claims, characterized in that

 - the porous carbon-containing substrate is doped with at least one dopant selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorus (P), vanadium (V), scandium (Sc), gallium (Ga), indium (In), germanium (Ge), tin (Sn), lead (Pb), arsenic (As), antimony (Sb), bismuth (Bi), and mixtures thereof, and/or
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 - the silicon particles are doped with at least one dopant selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorus (P), vanadium (V), scandium (Sc), gallium (Ga), indium (In), germanium (Ge), tin (Sn), lead (Pb), arsenic (As), antimony (Sb), bismuth (Bi), and mixtures thereof, and/or
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 - the at least one aqueous suspension additionally comprises at least one compound containing at least one dopant selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorus (P), vanadium (V), scandium (Sc), gallium (Ga), indium (In), germanium (Ge), tin (Sn), lead (Pb), arsenic (As), antimony (Sb), bismuth (Bi), and mixtures thereof, and/or
 - the at least one heat treatment is carried out in the presence of a process gas containing or consisting of nitrogen.
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12. A treated substrate comprising a carbon-containing substrate material having pores, the substrate having on at least one surface an infiltration zone in which the pores of the substrate material are at least partially filled with silicon carbide, wherein the treated substrate has a permeability of at most $5 \cdot 10^{-15} \text{ m}^2$ and wherein the treated substrate has an open porosity in the infiltration zone, determined by mercury porosimetry, of at most 10%.

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13. The treated substrate according to claim 12, characterized in that the treated substrate

 - has a permeability of not more than $1 \cdot 10^{-16} \text{ m}^2$, preferably not more than $1 \cdot 10^{-17} \text{ m}^2$, particularly preferably not more than $1 \cdot 10^{-19} \text{ m}^2$, and/or
 - has a permeability which is lower by a factor of at least 10, preferably at least 100, than a permeability of the substrate before the treatment, and/or
 - has an open porosity in the infiltration zone, determined by mercury porosimetry, of not more than 8%, preferably not more than 5%, and/or

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 - has an open porosity in the infiltration zone, determined by mercury porosimetry, which is lower by at least 7%, preferably by at least 10%, particularly preferably by at least 12%, relative to the total volume of the treated substrate, than an open porosity of the treated substrate outside the infiltration zone, and/or
 - has a resistivity of at most 1500 mΩcm, preferably at most 10 mΩcm, and/or
 - does not contain any elemental silicon.
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14. The treated substrate according to claim 12 or 13, characterized in that

 - the infiltration zone has an average thickness of at least 100 μm, preferably from 100 μm to 1200 μm, particularly preferably from 200 μm to 800 μm, and/or
 - the silicon carbide with which the pores of the substrate material in the infiltration zone are at least partially filled contains 3C-SiC, preferably has 3C-SiC as the main phase.

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- 15. The treated substrate according to any one of claims 12 to 14, characterized in that the carbon-containing material is selected from the group consisting of graphite, preferably iso-graphite; carbon fiber reinforced carbon; silicon carbide fiber reinforced carbon; silicon carbide fiber reinforced silicon carbide; sintered silicon carbide; glassy carbon; and combinations thereof.

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- 16. The treated substrate according to any one of claims 12 to 15, characterized in that the silicon carbide is doped with at least one dopant selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorus (P), vanadium (V), scandium (Sc), gallium (Ga), indium (In), germanium (Ge), tin (Sn), lead (Pb), arsenic (As), antimony (Sb), bismuth (Bi), and mixtures thereof, wherein the at least one dopant is preferably

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- selected from the group consisting of nitrogen (N), aluminum (Al), boron (B), phosphorus (P), vanadium (V), scandium (Sc), and mixtures thereof, and/or
 - is present in the infiltration zone in a concentration in the range from $1 \cdot 10^{10}$ atoms per cm^3 to $1 \cdot 10^{23}$ atoms per cm^3 , preferably in the range from $1 \cdot 10^{12}$ atoms per cm^3 to $1 \cdot 10^{21}$ atoms per cm^3 , particularly preferably in the range from $1 \cdot 10^{15}$ atoms per cm^3 to $1 \cdot 10^{18}$ atoms per cm^3 .
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17. The treated substrate according to any one of claims 12 to 16, characterized in that it is preparable or is prepared using a method according to any one of claims 1 to 11.
18. A use of a treated substrate according to any one of claims 12 to 17 as a component for high temperature furnaces, preferably heater, insulation component, support; as crucible or crucible element.